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Graphical abstract: Mechanism diagram for the synthesis of activated carbons from crab shell wastes.

1 **High surface area and oxygen-enriched activated carbon**

2 **synthesized from animal cellulose and evaluated in electric**

3 **double-layer capacitors**

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10 **Abstract**

11   Crab shell, an abundant food waste and high volume organic resource, has been

12 used to synthesize oxygen-enriched activated carbon. The thermal stability, surface

13 area, morphology and surface chemical composition were characterized by

14 thermogravimetric analysis, nitrogen adsorption, scanning electron microscope,

15 energy dispersive X-ray spectroscopy, Fourier transform infrared spectroscopy and

16 X-ray photoelectron spectroscopy. The obtained activated carbon had a high surface

17 area of 3442 m^2 g^{-1}, large pore volume of 2.327 cm^3 g^{-1} and rich surface oxygen

18 species of 18.50 at.%. The cyclic voltammogram, galvanostatic charge/discharge and

19 electrochemical impedance spectroscopy tests were performed to investigate the

20 electrochemical properties of resultant carbon electrodes. The specific capacitance

21 was 280.6 F g^{-1} at a current density of 0.2 A g^{-1} and still maintained as high as 233.4 F

22 g^{-1} even at a high current density of 10 A g^{-1}, indicating the great potential of crab

1   shell-activated   carbons   in   the   development   as   electrode   materials   for

2   high-performance supercapacitors.

3   **Keywords:** Activated carbon; Animal cellulose; High surface area; Oxygen-enriched;

4   Electrochemical properties

5   **1. Introduction**

6   There are huge amount of lakes and oceans all over the world, therefore the

7   production of crabs is enormous per year [1]. Crab shells (CS) are one of the most

8   common solid wastes in seafood industries. Based on up-to-date data, it is estimated

9   that the production of crab shell is over millions of tons annually and approximately

10   85% of crab shells are ultimately disposed in landfill, resulting in a serious

11   environmental problem. Owing to the strict environmental regulations, how to reuse

12   this solid waste in a proper manner and also create possible economic value to the

13   industries is significant. The raw crab shells are mainly composed of 40-60% calcium

14   carbonate, 20-27% chitin, 11-29% protein, 3-5% magnesium carbonate and some

15   lipids as dry weight basis [2-4]. Chitin, the second most abundant polymer in nature, can

16   be extracted from the shells by using very simple chemical treatments. Chitin is a

17   modified polysaccharide with a strictly hierarchical structure, which is consisted of

18   the units of N-acetylglucosamine [5]. Or rather, chitin could be regarded as one

19   hydroxyl group on per monomer of cellulose replaced by an acetyl amine group.

20   Chitin, also called animal cellulose, possess abundantly available carbon content and

21   various surface chemical groups. In addition, chitin in crab shell is often associated

22   with various types of proteins or lipids, which could also be employed as carbon

1   precursor.

2   Up to now, most researches have been only focused on the reutilization of crab

3   shells or chitin from crab shells as bioadsorbents to remove heavy metals [6-9].

4   Activated carbons (ACs) with high surface area, large pore volume and hierarchical

5   microporous/mesoporous structure are widely used in various fields, including

6   adsorption [10], gas separation/ storage [11, 12], catalysis supporter [13] and electric

7   double-layer capacitors (EDLCs) [14]. However, the commercial ACs derived from

8   relatively expensive and non-renewable starting materials such as coals, are high cost

9   and unjustified to the pollution control applications. Recently, various types of wastes

10   have proven to be good candidates for the synthesis of ACs, such as nut shell [15],

11   sludge [16], alkali lignin [17], lotus stalk [18], coal tar pitch [19] , rice husk [20] and

12   *Enteromorpha prolifera* [21]. Animal cellulose from crab shell wastes could also be an

13   available raw material for the synthesis of ACs.

14   According to literature reviews, no research has been reported on the preparation

15   of low-cost activated carbon from animal cellulose of crab shells. Therefore, the main

16   objective of this study was to explore the potential of crab shell wastes in the

17   synthesis of activated carbon with high surface area using potassium hydroxide as

18   activating agent. The physical/ chemical properties and electrochemical performances

19   of the obtained ACs were also investigated.

20   **2. Experimental**

21   **2.1. Preparation of activated carbon**

22   Raw crab shell wastes were collected from a crabmeat processing factory in Hebei,

1   China. The shells were sun-dried for several days and mechanically ground to

2   particles in size range of 0.074-0.15 mm. As shown in Fig. 1 and Fig. 2, the formation

3   process of the ACs from crab shells was carried out on a simple and reproducible

4   route. Firstly, the raw shell was treated with 1 N HCl at a solid-liquid ratio of 100 g

5   L^{-1} for 6 h followed by rinsing with distilled water several times. This pre-treatment

6   procedure was performed to guarantee the removal of excess minerals, like calcium

7   carbonate or calcium phosphate, on the shell surface [22, 23]. The obtained acidified crab

8   shell (ACS) was mainly composed of chitin and protein. Then, the ACS was dried in

9   an oven at 60 ^{o}C for 24 h and the weight loss in this process was found to be

10   approximately $55\pm1\%$. Secondly, the ACS was carbonized at 500 ^{o}C for 90 min. The

11   obtained char was denoted as CCS. The char yield in the carbonation process was 28

12   $\pm0.5\%$. Then the CCS was mixed with potassium hydroxide powder. The mixture

13   was transferred to a tube furnace and pyrolyzed under nitrogen flow at 800 ^{o}C for 60

14   min. After cooling under nitrogen protection, the sample was washed repeatedly with

15   HCl solution and distilled water to remove residual alkali and inorganic impurities.

16   Finally, the product was dried at 105 ^{o}C overnight and ground into powders. The

17   obtained product was designated as CSAC-x (x=1, 2, 3, 4 and 5), where x represented

18   the weight ratio between potassium hydroxide and char. The carbon yield in the

19   activation process was $24.5\pm1\%$. This preparation process was referred from our

20   previous work [21]. The synthesis process was carried out in triplicate and the average

21   result was obtained.

22   **2.2. Characterization**

1   Thermal gravimetric analysis (TGA) was performed using a thermogravimetric

2   analyzer (SHI-MADZU, TGA-50). Each analysis was carried out at a 100 mL min^{-1}

3   N_2 rate with a heat rate of 10 $^{\circ}$C min^{-1} from room temperature to 900 $^{\circ}$C. The pore

4   size distribution and surface area of the ACs were determined at 77 K using a surface

5   area analyzer (JW-BK122W). The surface physical morphology and mineral

6   components of the ACs were examined by using a scanning electron microscopy

7   (JEOL, JSM 7600F) and an energy dispersive X-ray spectroscopy (Oxford INCA

8   sightX). Fourier transform infrared spectroscopy (NICOLET 6700) and X-ray

9   photoelectron spectroscopy (ESCALAB 250) tests were carried out to investigate the

10   chemical properties of the samples.

11   **2.3. Electrochemical measurements**

12   All electrochemical characterizations of the CSAC-3 based electrodes were tested

13   in a symmetrical two-electrode configuration with 6 M KOH as electrolyte using an

14   electrochemical workstation (PARSTAT2273). To make a work electrode, the active

15   CSAC-3 powder, acetylene black and polytetrafluoroethylene (PTFE) were mixed in

16   ethanol with a weight ratio of 85: 15: 5. The mixture was coated onto nickel foam like

17   a sandwich with an area of 1 cm^2 and pressed under a pressure of 10 MPa. The

18   electrodes were dried in a vacuum oven at 100 $^{\circ}$C overnight. Approximately 2 mg of

19   active material was loaded in each electrode, and each electrode layer thickness was

20   50 μm. Electrochemical performances of the prepared carbon electrodes were

21   evaluated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and

22   electrochemical impedance spectroscopy (EIS). The potential window of CV curve

1   was set to be 0-1.0 V. In GCD test, different current densities from 0.2 to 10 A g^{-1}

2   were employed to evaluate the charge-discharge performance of the samples. The EIS

3   test was performed in the frequency ranges of 100 kHz to 100 mHz at an open circuit

4   potential of 10 mV. The specific capacitance based on CV and GCD measured was

5   calculated using the following equations:

6    $$C_{CV} = \frac{\int I du}{v m \Delta V}$$ (1)

7    $$C_{GCD} = \frac{I \Delta t}{m \Delta V} \times 2$$ (2)

8   where I is the current (A), u is the potential (V), v is the voltage scan rate (mV s^{-1}), m

9   is the weight of the active material in each electrode, ΔV is the total potential

10   difference (V) and Δt is the discharge time (s).

11   **3.   Results and discussion**

12   **3.1. Thermal analysis**

13   TGA analysis can provide useful information on thermal behavior of materials

14   through the study of characteristic decomposition patterns or degradation mechanisms.

15   Hence, TGA coupled with DTG analysis were employed in this study to gain suitable

16   temperature range for the carbonization and activation process. Fig. 3 exhibits the

17   TGA-DTG curves for both acidified crab shell and carbonized crab shell impregnated

18   with KOH. Both samples display three steps for weight loss, yet remarkable variations

19   could be discovered in the band locations and intensities. Fig. 3a shows that the

20   decomposition of the acidified crab shell was consisted of three stages, namely

21   dehydration, devolatilization and decomposition of carbonaceous substance, which

1 was different from pure chitin or protein [24, 25]. This result demonstrated that the

2 acidified crab shell was a combination of chitin, protein, lipid, ash and moisture,

3 which was in agreement with the previous study [23]. Furthermore, the shape of TGA

4 curve of acidified crab shell resembled like that of cellulose, implying that the

5 obtained acidified material could be used as a promising carbon precursor [26, 27]. The

6 first mass loss of 11.44% at 30-200 ^{o}C was caused by the evaporation of water

7 molecules, while the second mass loss observed in the temperature range of 200-408

8 ^{o}C was a result of the decomposition of chitin, protein or lipid molecules.

9 Approximately 53.03% weight of the sample was lost during this stage with two

10 significant DTG peaks at about 317.5 and 384.6 ^{o}C, which were similar to previous

11 studies [24, 25, 28]. In the third stage, from 408 to 800 ^{o}C, the sample release 15.77%

12 volatile substances and a char residue of 19.76% was gained. According to the above

13 analysis, the carbonization temperature was selected at 500 ^{o}C, because large

14 proportion of dehydration and devolatilization of raw materials occurred in this stage.

15   On the other hand, the raw precursor could be eroded by potassium hydroxide and

16 produced pores in the following aspects. (a) The primary surface dehydration

17 occurred, which could be deduced from the DTG peak at 77.2 ^{o}C (Fig. 3b). (b) The

18 secondary evaporation of internal water and partial polymerization of the raw

19 precursor were deduced from the DTG peak at 209.8 ^{o}C. (c) The raw precursor

20 transformed to char through aromatization reaction, which presented a high weight

21 loss between the temperature 100 and 750 ^{o}C. During this stage, the metallic

22 potassium coupled with some carbonates were produced to yield abundant fine pores

7

1   through intercalating to the carbon matrix [29]. (d) The progressive weight loss above

2   750 $^{\circ}$C was attributed to the decomposition of potassium carbonate into CO_2.

3   Therefore, the activation temperature was set at 800 $^{\circ}$C to ensure good development

4   of pores.

5   **3.2. Pore and microstructure characterization**

6   It can be seen from Table S1 that raising the impregnation ratio from 1 to 3 lead to

7   an increase in BET surface area from 1782 to 3442 m^2 g^{-1}, while further raising the

8   impregnation ratio from 3 to 5 resulted in a decrease in BET surface area from 3442

9   to 2188 m^2 g^{-1}. CSAC with the highest surface area was obtained at the impregnation

10   ratio of 3. Therefore, CSAC-3 was regarded as a typical sample for the following

11   investigation. As shown in Fig. 4a, the N_2 adsorption-desorption isotherms of

12   CSAC-3 presented a type I shape with somewhat type IV character. The isotherms

13   showed a significant adsorption of nitrogen at the relative pressure below 0.1,

14   indicating the presence of micropores. A slight hysteresis loop (or capillary

15   condensation) occurred at the medium relative pressure of 0.4-0.7, implying that

16   CSAC-3 possessed some mesopores. And the hysteresis loop belonged to H3/H4,

17   which was associated to the existence of slit-liked pores [30, 31]. The size of micropores

18   for CSAC-3 displayed a multimodal distribution nature with four different maxima at

19   0.55, 0.62, 0.74 and 0.83 nm (Fig. 4b). All textural parameters of CS, ACS, CCS and

20   CSAC-3 are presented in Table 1. The acidification and carbonization processes led to

21   slight change to the surface area and pore volume for raw precursor. However, the

22   surface area and pore volume increased to 3442 m^2 g^{-1} and 2.327 cm^3 g^{-1} after

8

1 activation. Compared with some previous studies [32-35], ACs prepared from crab shell

2 exhibited higher surface area than that of other raw precursors, such as sugarcane

3 molasses, sunflower seed shell, rice straw and *Argania spinosa* seed shells. The

4 average pore diameter for CSAC-3 was 2.704 nm and the ratio of mesopores/ total

5 pores reached 90.46%. As displayed in Fig. 4b, most pores were intensively

6 distributed in the pore range of 2-4 nm. According to the previous study, large surface

7 area and high proportion of mesopores for ACs facilitated the access of electrolyte

8 ions into the pores, contributing to good electrochemical performances in EDLCs [36,

9 37].

10 Scanning electron microscopy equipped with EDX was carried out to analyze the

11 morphologies and components on the surface of CS, ACS, CCS and CSAC-3. In EDX

12 analysis (Fig. 5), strong Ca peaks could be observed on virgin crab shell surface,

13 which confirmed that the shells contained calcium carbonate. Other peaks

14 corresponding to Na, Mg, P, Cl, K, Cu, Mn and Pb were also recorded in the EDX

15 spectrum (Table S2). It is interesting to find that the calcium peaks decreased

16 remarkably after acidification, implying that the calcium leached out from the shells

17 successfully through demineralization. SEM images showed that the surface of virgin

18 crab shell display lamellar-like structure with many straightly tunnel-like and striped

19 trench (Fig. 6a and Fig. S1a). After acidification treatment, the ACS surface exhibited

20 apparent microfibrillar crystalline structure in a sequence of hierarchical layer patterns,

21 indicating that the reserved main constituents contained chitin (Fig. 6b and Fig. S1b).

22 Other previous researchers also found that the purified crab shell displayed similar

1 microfibrillar structure [5, 38]. After carbonization, the surface became smooth with

2 plate-like stripes (Fig. 6c and Fig. S1c). After activation, the surface of the resultant

3 sample presented abundantly flower-like or honeycomb-like 3-D pore network

4 skeleton (Fig. 6d and Fig. S1d).

5 **3.3. Chemical characterization**

6 The electrochemical behaviors of EDLCs not only rely on the physical properties

7 but also on surface chemical characteristics, hence FTIR and XPS were used in this

8 study. Fig. 7 revealed five different characteristic bands for CS, ACS, CCS and

9 CSAC-3. These bands were: 3425 cm^{-1} (O-H stretching vibration), 2910 cm^{-1} (C-H

10 stretching), 1648 cm^{-1} (C=O secondary amide stretching), 1425 cm^{-1} (C-H

11 deformation) and 1060 cm^{-1} (O-C-O asymmetric stretching in phase ring) [24, 39], which

12 became weaken, shifted or disappeared for CSAC-3, indicating that the hydrogen

13 element was removed to a large extent due to the dehydration or pyrolyzation reaction

14 during activation process. The surface elemental compositions of the prepared carbon

15 were further evaluated by XPS, listed in Fig. S2. It can be seen that the C1s spectrum

16 could be deconvoluted into three components, corresponding to: graphite type (284.6

17 eV), carbon in phenolic, alcoholic, etheric groups (285.6 eV) and carbon in carboxyl

18 or ester groups (288.7 eV) [39, 40]. The O1s spectra could be resolved into three

19 individual component peaks: oxygen in hydroxyl or metal oxides (530.6 eV), oxygen

20 doubly bonded to carbon (532.4 eV) and oxygen singly bonded to carbon in aromatic

21 rings, phenols and ethers (533.1 eV) [40, 41]. According to the area-simulating curve, the

22 relative percentage of each component was calculated and summarized in Table 2.

1   The relative content of oxygen in aromatic rings, phenols and ethers was 7.60%,

2   which was very high. According to the previous studies, CO-type functional groups

3   on the surface of ACs, including hydroxyl, quinine, phenols, ethers and carbonyl

4   groups, had a positive contribution to the specific capacity of carbon electrodes [42-44].

5   Since large numbers of O-enriched functional groups could not only promote the

6   wettability of carbon material, thus favouring the electrolyte ions to contact with the

7   pores, but also provide an additional pseudocapacitance due to a faradic process

8   involving the oxygen groups [42, 43].

9   **3.4. Electrochemical behavior**

10   Fig. 8a presents the CV curves of CSAC-3 electrodes at various scan rates of

11   10-100 mV s^{-1} in 6 M KOH aqueous electrolyte. The CSAC-3 electrodes displayed

12   good rectangular shapes, exhibiting almost mirror images with reference to the

13   zero-current line, which was a typical characteristic of the EDLCs. Furthermore, the

14   rectangular degree of the curves presented the ion diffusion rate into the pores of the

15   electrodes, and the higher rectangular degree reflects bigger ion diffusion rate [36].

16   Hence, the high rectangular degree of CV curves at high scan rates in this study

17   corresponded to the good ion transfer properties of the CSAC-3 electrode materials. It

18   is well-known that the RC time constant (τ) of the electrode is an important influence

19   factor on the voltammogram shape. The larger the constant time is, the longer the

20   transient part (less steepness of the CV curves at the switching potential) will be,

21   which signifies worse collapse of the rectangular profiles [37, 45, 46]. In addition, this

22   phenomenon usually becomes more prominent at higher scan rates. In this study, the

1 CV curves still maintained a good box-like shape at high scan rates, which implied

2 that the carbon electrode had small constant time as a desired capacitor with an

3 excellent capacitive ability. The RC time constant is only 5.01 s, which indicated that

4 the CSAC-3 electrode was suitable for higher power delivery.

5   The galvanostatic charge/discharge measurement at different current densities was

6 further employed to explore the electrochemical behaviors of the electrode materials.

7 All galvanostatic charge/discharge curves show almost isosceles triangular in shape

8 even at high current density of 2.5 A g^{-1} (Fig. 8b), suggesting an ideal electrochemical

9 reversibility of the electrodes. Additionally, the specific capacitance of CSAC-3

10 electrodes was 280.6 F g^{-1} at a current density of 0.2 A g^{-1} and still remained as high

11 as 233.4 F g^{-1} when the current density increased up to 10 A g^{-1} (Fig. 8c), which is

12 comparable to those reported elsewhere [19, 20, 37, 45]. The decrease of the capacitance

13 mainly derived from ohmic drop or high polarization of electrode at high current

14 density, which could result from the weakening accessibility of ions into the pores of

15 electrode matrices with the increasing current density [36]. The high capacitance

16 retention of 83% reflected an excellent rate capability of the electrodes.

17   To evaluate the effects of frequency on the power performance of CSAC-3

18 electrodes, the prepared carbon electrodes were investigated by electrochemical

19 impedance spectroscopy. As shown in Fig. 9 a, the Nyquist plot consist of three parts:

20 (a) a semicircle at high frequency region, which was correlated to the resistance of the

21 CSAC-3 electrode itself as well as the contact resistance between CSAC-3 electrode

22 and current collector. During this stage, the value of capacitance was almost zero and

1   the system behaved like a pure resistor (Fig. 9b). Because scarcely any charge transfer

2   complexes could overcome the activation energy to move with the quick changes of

3   the potential; (b) a 45° Warburg line at middle frequency region served as a knee or

4   transition between the semicircle and vertical line; (c) a vertical line at low frequency

5   region implied a pure capacitive electric double layer capacitor behavior [31, 36]. The

6   data of Nyquist curve was fitted by using the ZSimpWin software based on the

7   equivalent circuit (Fig. 9a inset). The equivalent series resistance of the electrode was

8   0.194 Ω, which made it possible for high power performance. The excellent

9   electrochemical performance of CSAC-3 electrode may attribute to the characteristics

10   of the crab shell carbon materials. Firstly, large specific surface area provided

11   sufficient electrode/electrolyte interface sites for charge storage. Secondly, dominant

12   mesopores in the porous carbon material resulted in low inner-pore ion-transport

13   resistance and diffusion distance, which facilitated the electrolyte ion to transfer and

14   access into the internal pores quickly [37, 47]. Thirdly, the presence of abundant

15   oxygen-contained groups enhanced the surface wettability of the electrode surface,

16   affording more exposed surface for charge accommodation.

17   **4. Conclusions**

18   Novel oxygen-rich activated carbons were fabricated by KOH activation using

19   animal cellulose withdrawn from crab shell wastes as precursor and applied as

20   electrode materials. The obtained carbon materials presented outstanding performance

21   as an EDLC electrode owing to large specific surface area of 3442 m^{2} g^{-1}, high

22   mesopores ratio of 90.46% and high oxygen content of 18.50%. The advantages of the

1 raw material were: (1) abundantly available and cheap; (b) instinctively high oxygen

2 content; (c) simple and cost-effective synthesis; (d) good electrochemical performance.

3 This investigation provides an interesting and promising candidate for supercapacitor

4 industry.

5 **Appendix A. Supplementary data**

6 Supplementary data related to this article can be found, in the online version, at

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1 **Figure captions**

2 Fig. 1. Flow diagram for the synthesis of activated carbons from crab shell wastes.

3 Fig. 2. Mechanism diagram of for the synthesis of activated carbons from crab shell

4 wastes.

5 Fig. 3. TGA and DTG curves for the pyrolysis of (a) acidized crab shell and (b)

6 carbonized char impregnated with potassium hydroxide.

7 Fig. 4. (a) N_2 sorption/desorption isothermals and (b) pore size distribution curves

8 (inset: micropore size distribution) of the prepared carbons.

9 Fig. 5. EDX spectrum (a) raw crab shell and (b) acidized crab shell.

10 Fig. 6. Scanning electron microscopy image of (a) raw crab shell, (b) acidized crab

11 shell, (c) carbonized crab shell and (d) crab shell activated carbon (×20000).

12 Fig. 7. FTIR spectra of (a) raw crab shell, (b) acidized crab shell, (c) carbonized crab

13 shell and (d) crab shell activated carbon.

14 Fig. 8. (a) Cyclic voltammograms at different scan rates, (b) charge/discharge curves

15 and (c) the specific capacitance at various current densities of CSAC-3 electrodes.

16 Fig. 9. (a) Nyquist impedance plots and normalized real and imaginary part

17 capacitance of the CSAC-3 electrodes.

18 Fig. S1. Scanning electron microscopy image of (a) raw crab shell, (b) acidized crab

19 shell, (c) carbonized crab shell and (d) crab shell activated carbon (×5000).

20 Fig. S2. C 1s and O 1s XPS spectra of CSAC-3.

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1   Table 1

2   Porous structure parameters of crab shell, acidized crab shell, carbonized crab shell and crab shell

3   resulting activated carbon.

Parameters	CS	ACS	CCS	CSAC-3
BET surface area (m^2 g^{-1})	1.817	5.061	10.45	3442
Total pore volume (cm^3 g^{-1})	0.030	0.017	0.033	2.327
t-method micropore volume (cm^3 g^{-1})	0.000	0.000	0.000	0.642
BJH method mesopore volume (cm^3 g^{-1})	0.033	0.019	0.036	2.105
Average pore diameter (nm)	65.479	13.753	12.744	2.704

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1　　Table 2

2　　Relative content of the surface functional groups determined from the XPS analysis.

Peaks no.		Binding energy (eV)	Surface group	Assignment	Relative content (%)
C1s	Peak 1	284.6	C	Graphitic carbon	35.92
	Peak 2	285.6	C-O-	Phenolic, alcoholic, etheric	20.10
	Peak 3	288.7	COO	Carboxyl or ester	24.21
O1s	Peak 1	530.6	O/OH-	Hydroxyl or metal oxides	0.63
	Peak 2	532.4	C=O	Oxygen doubly bonded to carbon	10.27
	Peak 3	533.1	C-O-	Aromatic rings, in phenols and ethers	7.60
N1s	Peak 1	400.2	C-N-C	Pyrrolic nitrogen, pyridones or a mixture of both	1.27

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Fig. 1. Flow diagram for the synthesis of activated carbons from crab shell wastes.

Fig. 2. Mechanism diagram for the synthesis of activated carbons from crab shell wastes.

Fig. 3. TGA and DTG curves for the pyrolysis of (a) acidized crab shell and (b) carbonized char impregnated with potassium hydroxide.
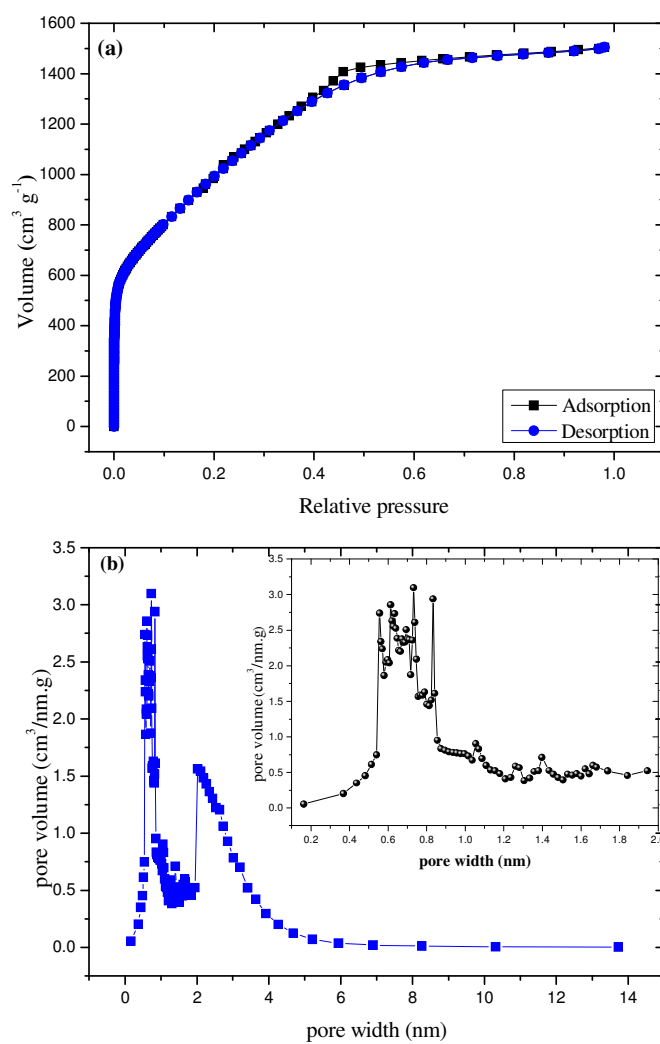
Fig. 4. (a) N$_2$ sorption/desorption isothermals and (b) pore size distribution curves (inset: micropore size distribution) of crab shell activated carbon.
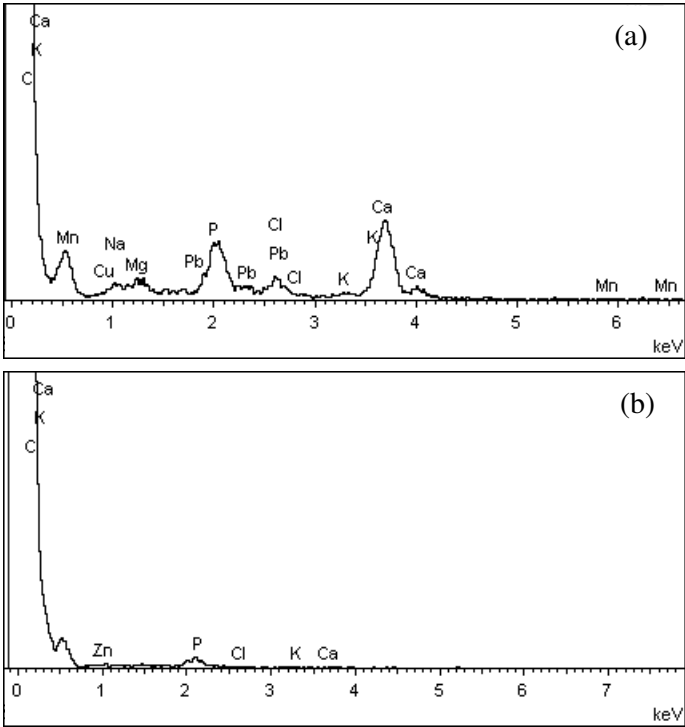
Fig. 5. EDX spectrum (a) raw crab shell and (b) acidized crab shell.

Fig. 6. Scanning electron microscopy image of (a) raw crab shell, (b) acidized crab shell, (c) carbonized crab shell and (d) crab shell activated carbon (×20000).

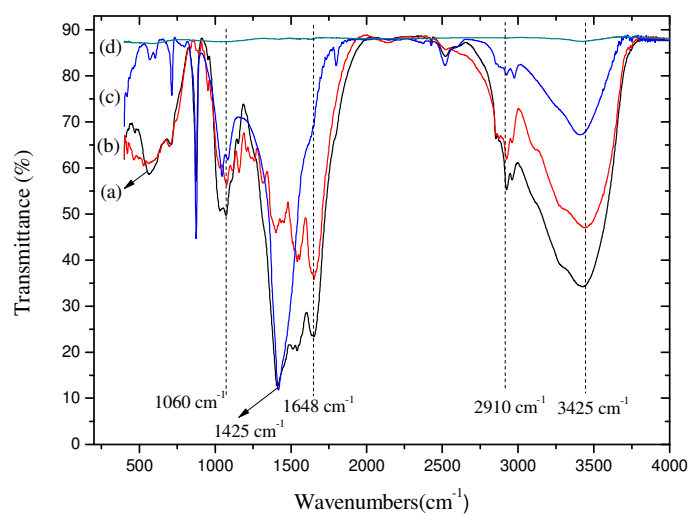Fig. 7. FTIR spectra of (a) raw crab shell, (b) acidized crab shell, (c) carbonized crab shell and (d) crab shell activated carbon.
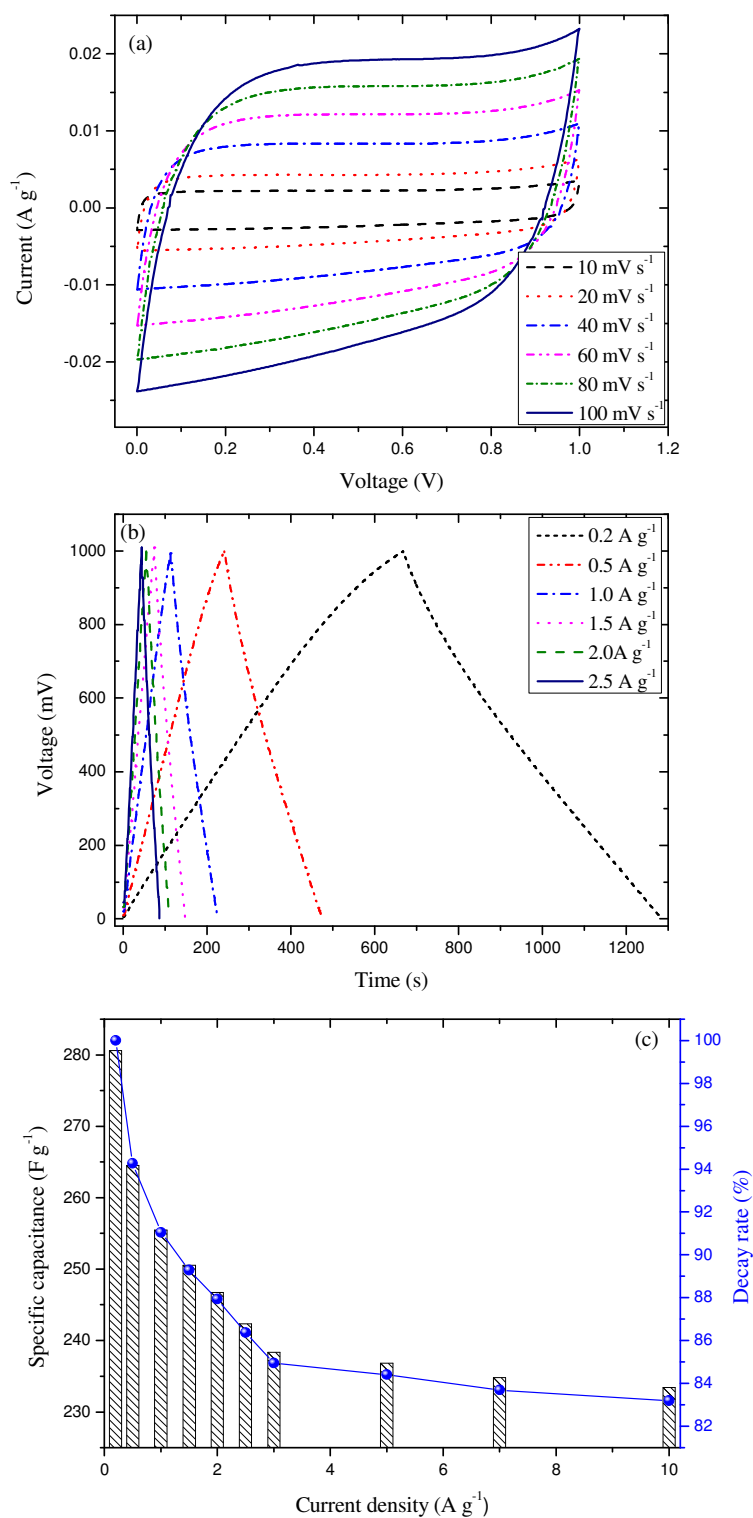
Fig. 8. (a) Cyclic voltammograms at different scan rates, (b) charge/discharge curves and (c) the specific capacitance at various current densities of CSAC-3 electrodes.
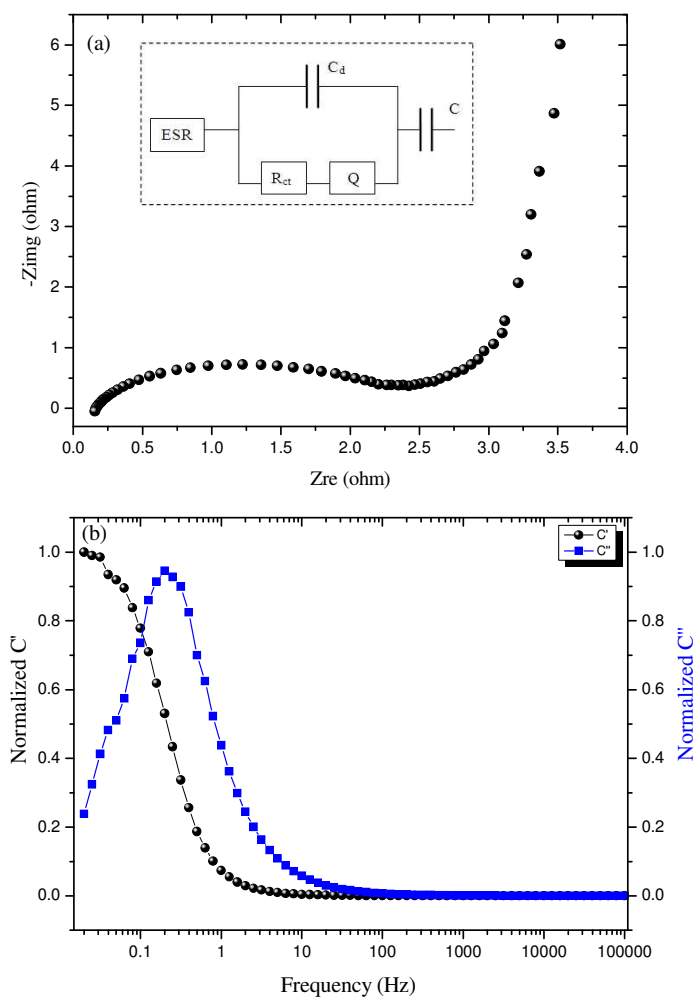
Fig. 9. (a) Nyquist impedance plots and normalized real and imaginary part capacitance of the CSAC-3 electrodes.