Synthesis of Nanoporous Carbon with New Activating Agent for high-performance Supercapacitor

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Abstract:

In the present work, we report a new activating agent (NaCl: KCl) (1: 1) for the synthesis of nanoporous carbon from Java Kapok tree shell (1:1) with different controlled temperature under inert atmosphere. Additionally, surface morphology, physico-chemical and electrochemical properties of the nanoporous carbon are characterized. The obtained Kapok shell derived nanoporous carbon possessed a large surface area of 1260 m^2 g^{-1}, pore volume of 0.439 cm^3 g^{-1}, pore size of 1.241 nm, and microspore volume of 0.314 cm^3 g^{-1}. The nanoporous carbon-based electrode material exhibited higher capacitance of 169 F g^{-1} with 97% capacity retention after 10,000 cycles at $1Ag^{-1}$. We believe that this new activation agent can be significant contribution in the new carbon technology for energy storage materials.

Keywords: Biomass, Activated Carbon, Cyclic Voltammetry, Supercapacitors

Graphical abstract

Figure- Schematic illustration kapok shell derived nanoporous carbon formation.

1. Introduction

In general, porous activated carbon, CNT, graphene are prepared by carbonization of carbon precursor and sequential chemical activation (KOH, NaOH, K_2CO_3, HCl,Mg/Zn, $ZnCl_2$ or H_3PO_4 etc.,) and physical activation (CO_2,NO_2,Ar,H_2O, air or microwave etc.,)[1, 2]. Due to large specific surface area, high porosity, conductivity, energy, long cycle and temperature stability [3], the activated carbon is usually applied in many fields, such as supercapacitors [4, 5] lithium ion anodes [6], sodium ion anodes and CO_2 capture [7]. Amongst many varieties of carbon precursor, the biomass-derived activated carbon is a kind of economical and advantageous material because of low cost, environmentally friendly and high performance. Because of its high surface area, extensive porosity and the profuse surface functional groups, the porous activated carbon can make the electrode material store more counter-ions electrostatically in the diffuse layer formed next to the surface and lead to a higher electrical double layer capacitance [8].

In this present work, we consider the environmental solicitude and mainly focus on the consumption of energy from bio-waste. The nanoporous carbon from the biomass of Java kapok, (Ceiba pentandra), also called Java cotton. Kapok tree shell was obtained from fruit of the kapok and it is a cheap, most abundant, sustainable biological resource. The synthesis of molten salt solution is based on multi-salts with low melting point. In this work, new activating agent, molten salt (NaCl: KCl) solution with low melting point of 657°C is employed for the synthesis of highly nanoporous carbon from biomass. To the best of our knowledge, influence of molten salt as activating agents on the surface morphology and electrochemical properties of activated carbon made from kapok has not been investigated. The major objective of this study is to synthesis nanoporous carbon with novel activating agent from kapok.

2. Experimental

The received Kapok tree shell was first washed to remove all cottons, seeds, mud and impurities. The Kapok tree shell was then carbonization at 300 ^{0}C for 2hours in the muffle furnace. Further it was cooled for 24 hours and thus the carbonized powder was crushed into fine powders by ball milling and collected for further activation. In the next process, sodium chloride (NaCl) and potassium chloride (KCl) salt (molten salt) is mixed at the ratio of 1:1.This molten salt solution was used as solvent and activating agent. 10 g of carbonized powder was mixed with 10 g of activating agent using distilled water and stirrer at 70°C until water evaporated. Then, it was dried at 120 °C for 24 hours to expel the moisture.

After drying, the carbon is activated at different temperatures of 800 °C, 900°C, 950 °C and 1000°C for 1 hour under nitrogen gas flow rate of 80 cm^3 min^{-1}. Then, it was treated with excess of diluted hydrochloric acid and repeatedly washed with distilled water until chloride ions are expelled. It is then dried at 120 ^{0}C for overnight in a hot air oven to remove the moisture content. The carbon activated at 800 °C, 900°C, 950 °C and 1000°C is referred to as KNPC800, KNPC900, KNPC950 and KNPC1000 respectively.

3. Results and discussion

The TGA/DTA curves are shown in **Fig. 1(a)**. The TGA curves of kapok shell raw material, carbonized Kapok shell at 300°C and KNPC 1000 respectively were compared. The TGA curves reveal a higher weight loss (55%) between 230 ˚C to 350˚C which represents the degradation of volatile substances and removal of oxygen functional groups from the surface. Hence, 300 ˚C kept as the standard temperature for carbonization. For 300°C carbon, the activation appeared around 550°C and after that there is certain amount decrease in the weight (24%), thus few more functional groups may be removed. In KNPC 1000, there is linear and stable decomposition

occurred. Hence, it indicates the better removal of the functional groups at900°C. This is clearly depicted in DTA with two broad peaks at 75.35˚C and 889.07˚C, respectively. These endothermic peaks denoted the phase transition of samples shown in **Fig. 1(b)**.

The FE-SEM images of KNPC 1000 ^{0}C is shown in **Fig. 1(c).** TheKNPC-100 shows hallow structured morphology with more pores generated during carbonization. The HR-TEM image of KNPC-1000 is shown in **Fig. 1(d)**. These results show the enhancement of microstructures, and considerably encompassed of highly oriented pores randomly noticed in the structure.

It is suggested that the activation of carbon with KCl:NaCl proceeds as the following mechanism. During the pyrolysis, the molten salt (NaCl-KCl) produces the dehydrating effect to the lignin; cellulose and hemicelluloses present in the biomass and facilitates bonding between them. The dehydration produced by the molten salt at the eutectic temperature greater then 657oC produces reduction in the dimension of the particle. Such reductions are partially inhibited by remaining reactant inside during pyrolysis thus it acting as a template for the creation of porosity. Thus the pores created as small and uniform size is due to the small size of the molten salt.

The X-ray diffraction (XRD) patterns of KNPC800, KNPC900, KNPC950 and KNPC1000 are shown in **Fig. 2(a).** The XRD patterns exhibits two broad peaks around 21-25° and 43°, which gives the crystallographic planes (002) and (100) in the carbon structure. All broad peaks (002) confirm the amorphous nature of the obtained KNPC. The temperature and the graphitic nature is directly proportional to each other (i.e.) as temperature increases, the graphitic nature is also increases. The plane (002) increases from 21.4^0 to 24.1^0. From the table-1, clearly indicate increase the temperature proposing the increase of the graphitic nature of the carbon (002) direction increase from 21.4^0 to 24.15^0. The KNPC1000 exhibits two broaden diffraction peaks

appear around 24.1° and 43.8° which corresponds to the (002) and (100) plane representing the partially graphitic nature.

The Raman spectra **Fig. 2**(b) exhibits three notable peaks related to graphene structure in D band1351cm^{-1}(defect and disordered carbon), G band1582 cm^{-1}(graphitic carbon) and the 2D band at 2434cm^{-1}. As carbonization temperature increases, the G band and D band intensity increases and the integrated strength ratio (I_g/I_d) increase. The I_g/I_d ratios of KNPC 800, KNPC 900, KNPC 950, and KNPC 1000 were 1.69, 1.75, 1.86 and 2.29, respectively. Similarly I_{2d}/I_g ratio surged till 950 ^{0}C and dropped after 1000 ^{0}C from 1.27 to 0.38. This also indicates that the increase in temperature favors the formation of graphitic nature.

The nitrogen gas adsorption-desorption isotherms measurements of KNPC 1000 is shown in **Fig. 2(c-d)**. The results of the KNPC1000 possessed a microspore volume of 0.312 cm^{3}g^{-1}, microspore area of 596.106 m^{2}g^{-1}, pore volume of 0.439 cm^{3}g^{-1}, pore size of 1.241 nm and surface area (BET) of 1260 m^{2}g^{-1}.

The electrochemical properties KNPC1000 was tested in symmetrical electrode set up and it was polarized to 1.6 V with 6 M KOH as electrolyte. **Fig. 3**(a) denotes the CV curves at the scan rate of20 mVs^{-1}. The higher capacitance 169 Fg^{-1} was found at 1V and lower capacitance 122 Fg^{-1} at 1. 6 V. The Cyclic voltammetry at a different scan rates of 20 mV s^{-1}, 50 mV s^{-1},100 mV s^{-1}, and 200 mV s^{-1} at 1V, are shown in **Fig. 3(b)**. It reveals excellent capacitances as 169 Fg^{-1},156 Fg^{-1},148 Fg^{-1}and 139 Fg^{-1}, respectively. The CV curve at higher scan rate of 200 mV s^{-1} retains the rectangular shape and high capacitances were obtained, which corresponds to the fast charge-discharge process.

Two electrode galvanostatic charge/discharge of KNPC1000 full cell system with 6 M aqueous KOH electrolyte at different current rates of1 A g $^{-1}$, 2 A g $^{-1}$, 5 A g $^{-1}$, 10 A g $^{-1}$are shown in

Fig. 3(c) The calculated capacity are 169 Fg^{-1},158 Fg^{-1},147 Fg^{-1} and 142 Fg^{-1}, respectively and they are found to be decreasing. However, there is no significant voltage drop and higher capacitance at different current densities. These results thus demonstrate the remarkable rate capability of the KNPC1000 electrode. **Fig. 3**(d) reveals the comparison of all KNPC discharge capacitance with life cycle. We noticed the maximum specific capacitance of 169 Fg^{-1} with 97% retention after 10000 cycle's at 1 A g $^{-1}$. The maximum energy density of 12.5 Wh kg^{-1} and power density of 1.9 kWkg^{-1} were found at 1V.

4. Conclusion

The activated carbon from the Java Kapok tree waste is prepared with new activating agent of molten salt (NaCl- KCl) with high specific surface area of 1260 m^{2}g^{-1}. The specific capacitance was found to be 169 F g^{-1}with the capacitance retention greater than 97% after 10000 cycles. This novel activated carbon can be more economical and breakthrough technology for carbon materials and applications.

5. References

[1] R. J. White, V. Budarin and R. Luque, Chem.Soc.Rev. 38, (2009), 481-494.

[2] E. Senthilkumar, V. Sivasankar, Ravindra Kohakade. B, K. Thileepkumar, M. Ramya, G. Sivagaami Sundari, S. Raghu, R.A. Kalaivani, APSUSC ,S0169-4332 (2017) 33197, 1-5

[3] L. Hao, X. L. Li and L. J. Zhi, Adv. Mater. 25, (2013), 1-6.

[4] S. Y. Gao, Y. L. Chen, H. Fan, X. J. Wei, C. G. Hu, H.X. Luo and L. T. Qu, J. Mater. Chem. A.2, (2014), 1-4

[5] J. C. Wang and Q. Liu, RSC Adv. 5, (2015), 1-3

[6] X. Y. Zhou, J. J. Tang, J. Yang, J. Xie and B. Huang, J. Mater. Chem. A.1, (2013), 1-6

[7] N. P. Wickramaratne and M. Jaroniec, J. Mater. Chem. A. 1, (2013),112-115.

[8] A. C. Tas, Molten salt synthesis of calcium hydroxyapatite whiskers. Am. Ceram.Soc.84, (2001), 295-300.

Table 1. Result of XRD as well as Raman results of the nanoporous carbon materials.

Kapok shells derived nanoporous carbon samples at different temperature	I_D/I_G ratio	I_{2D}/I_G ratio	d_{002} Spacing (A^o)	Thickness in (002) plane (degree)
KNPC 800	1.69	0.93	4.15	21.4
KNPC 900	1.75	1.16	4.09	21.7
KNPC 950	1.86	1.27	4.05	21.9
KNPC 1000	2.29	0.38	3.6	24.15
I_D/I_G- I_D and I_G are the integrated intensities of the D and G bands, respectively, **I_{2D}/I_G-**I_{2D} and I_G are the integrated intensities of the 2D and G bands, respectively. **d_{002}-** Interplanar spacing. **(A^o)**				
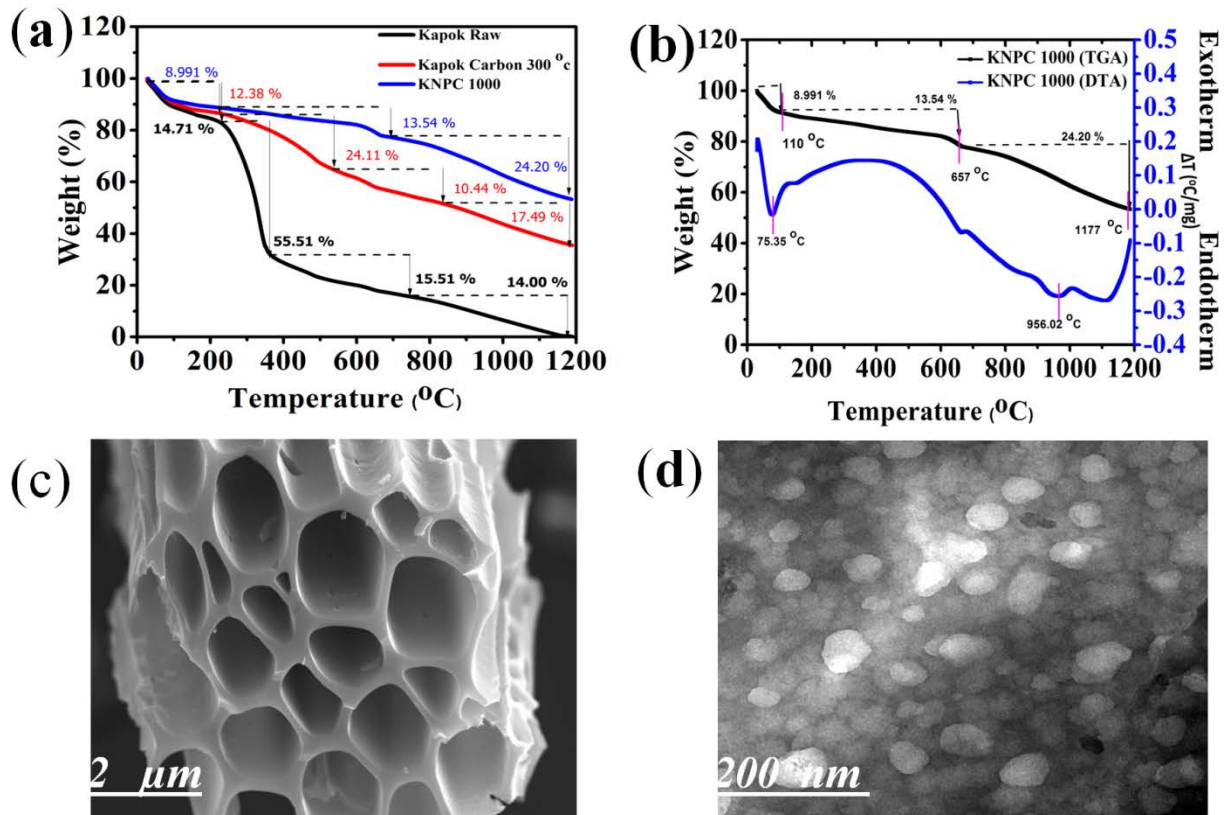
Figure 1.a). TGA comparison of raw material, 300°C carbon material and KNPC 1000 nano pores carbon b). TGA-DTA for the KNPC 1000. c).FESEM image of KNPC1000 nano pores carbon d). HRTEM image of nano pores carbon derived from Kapok shell with molten salt treatment.
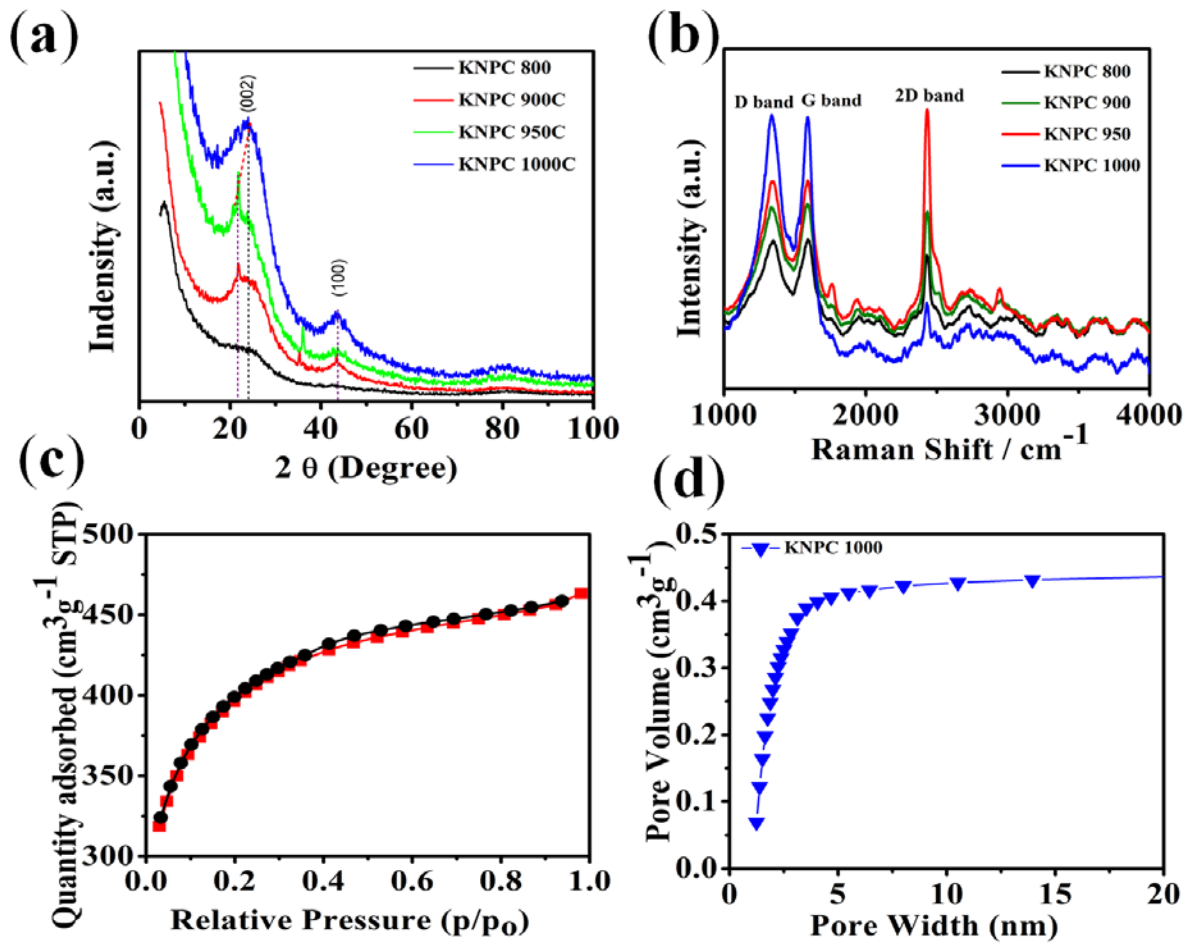
Figure 2.a). XRD pattern and b). Raman spectra normalized by the peak at temperatures ranging from 800−1000 °C for 1h. c). carbon di oxide adsorption–desorption isotherms of Molten salt activated nano porous carbon material, its indicating uniform microporous structure. d).Pore size distribution.
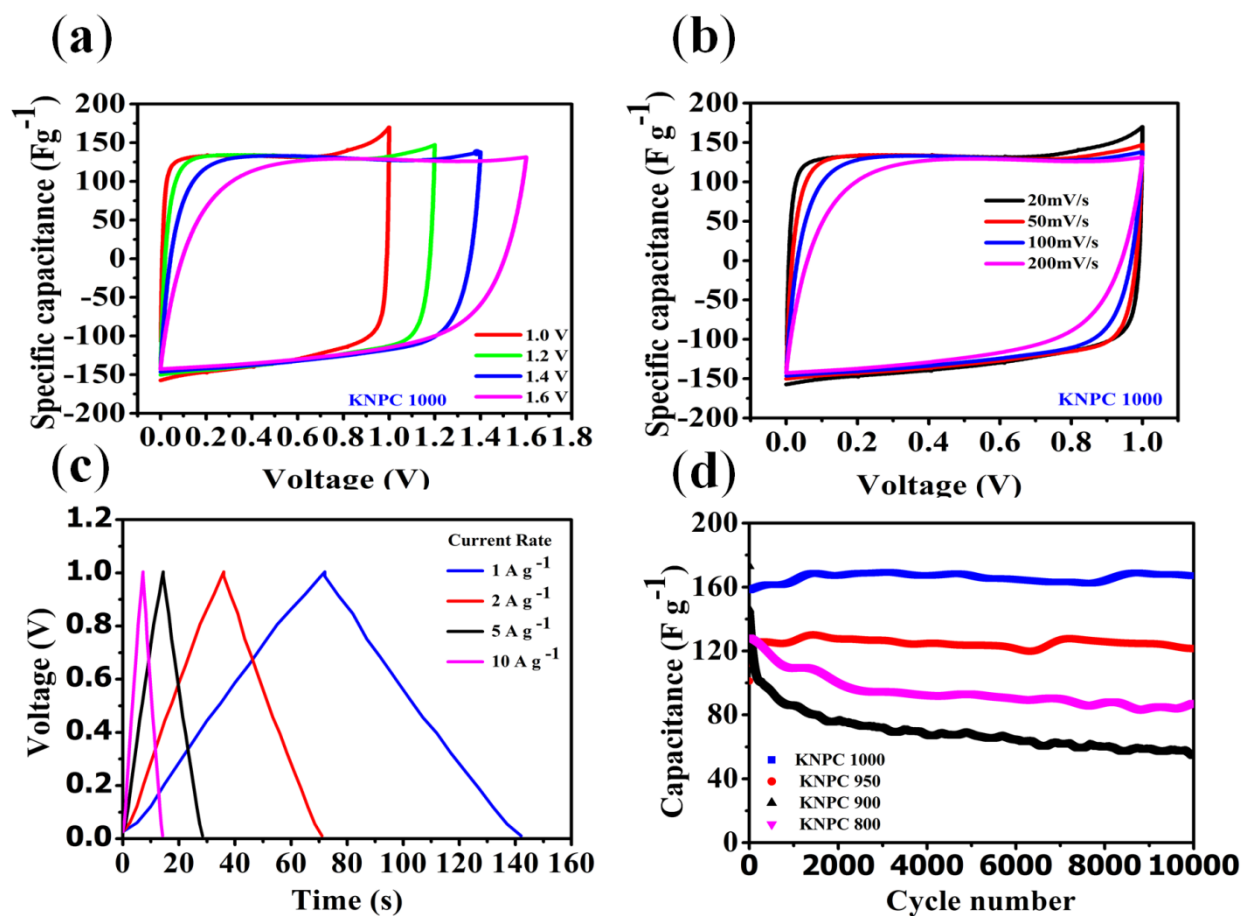
Figure 3.a) CV in different voltage (1V to 1.6V) b). CV curves of ECs with voltage scanning rates ranging from 20 mV S^{-1} to 200mV S^{-1} c). Galvanostatic cycling at a current rate of 1 Ag^{-1}. d). Long-term cycling performance of KNPC 1000 supercapacitors in KOH electrolytes at a current density of 1 Ag^{-1}: capacitance and Columbic efficiency vs. cycle number.