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Activating Agents Control the Morphology of Activated Carbon Materials from Biomass

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Abstract

The stems of the plant Calotropis gigantea (Cg) were were used as a feedstock for the activated carbon material. Carbonate (K_2CO_3) and oxalate ($Na_2C_2O_4$) were used as chemical activating agents. The morphological features of the activated carbon materials were characterized using FEG-SEM. The morphology of the activated carbon materials is found to depend on the type of activating agent used. Peculiar morphological features were observed in the activated carbon materials produced using the stems of Calotropis gigantea (Cg), as the sustainable feedstock, with two activating agents, namely carbonate and oxalate. Carbonate (K_2CO_3) activation resulted in graphene like, single layer activated carbon material of nanometer thickness, with uniform and well aligned spherical pores. In sharp contrast, with the same carbon feedstock, oxalate ($Na_2C_2O_4$) activation yielded activated carbon material of tubular (bundles of fused micro tubes) morphology. The sharp and striking contrast in the porous architecture at the nanoscale is attributed to the difference in the mechanism of activation with the nature and type of the activating agents, inorganic (carbonate) and organic (oxalate) activating agents. The morphological aspects of the activated (either by carbonate or oxalate) carbon materials derived from biomass (Cg) were compared with commercial activated carbon materials (Black Pearl 2000, Vulcan XC 72 R and CDX 975) derived from biomass. Unlike, the fine tenability and control of morphology attained with the activated carbon material from biomass, the surface morphology of commercial activated carbon materials comprised of nanospherical particles. Thus the tailorability and tunability of surface morphology of activated carbon materials by the judicious choice of the activating agents is exemplified.

Keywords: *Calotropis gigantea,* activating agents, chemical activation, carbonate, oxalate, morphology, graphene, carbon tubes, biomass

INTRODUCTION

Calotropis gigantea (Figure 1) is the plant with diverse applications. The fibre from the fruit of *Calotropis gigantea* is used as a textile fabric similar to cotton [1]. The roots of the plant are useful for the accumulation and removal of radio nuclides like ^{90}Sr and ^{137}Cs (Phytoremediation) from nuclear waste streams [2]. The ash from the seeds of the plant is used for the treatment of asthma [3]. The flower extracts of the plant are used as potential analgesic [4]. The root extract of the plant is used as contraceptive [5]. The stems of the plant are used for the preparation of activated carbon materials [6].

In general, activation is known to generate and develop (in volume and size) the porosity in the carbon material. As a result of activation the adsorptive capacity of carbon materials increases. A

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cluster of activating agents has been extensively employed for the production of activated carbon materials with desired pore structure. All the available methods of activation can be classified into two types, namely, physical activation and chemical activation depending on whether a gaseous or solid (and liquid) activating agent is used. Each of these methods has their own merits and demerits [7-10]. Activators like, alkali metal hydroxides (KOH) [11, 12], alkali metal carbonates (K_2CO_3) [13-17], transition metal salts ($ZnCl_2$) [18], alkaline earth metal salts ($CaCO_3$, $MgCO_3$) [19, 20], and mineral acids, such as, H_3PO_4 [21], HNO_3 [22], and H_2SO_4 [23], have been extensively exploited for the chemical activation of carbon materials. Though, often considered less advantageous, physical activation methods too, based on steam [24], air [25] and CO_2 [26] as activating agents have proven to be useful for the activation of carbon materials.

The objective of this original research article is to elucidate the possibility of fine tuning and controlling the surface morphology of activated carbon material from biomass (*Calotropis gigantea* stems are chosen as a representative example) using two different classes of activating agents namely, inorganic (K_2CO_3 is chosen as the representative example) and the organic ($Na_2C_2O_3$ is chosen as the representative example).

EXPERIMENTAL

Materials

The stems of *Calotropis gigantea* (Cg) were obtained from the campus of IIT Madras and subjected to systematic chemical treatments to obtain the activated carbon materials. Commercial activated carbon materials, namely, Black Pearl 2000, Vulcan XC 72 R were purchased from Cabot corporation, USA. The activated carbon material, namely, CDX 975 was generously provided by Ms Columbian Chemicals Company, USA. The chemicals used for the activation of the biomass feedstock, namely, K_2CO_3, $Na_2C_2O_4$, HCl, and NaOH were procured from Sisco Research Laboratory, India and were used as received without any further purification.

Methods

Synthesis of carbon material (char) from Calotropis gigantean [6, 27]

The dried stems of *Calotropis gigantea* (Cg) were employed as carbon precursor. A known amount of dried stems of plant was heated in a muffle furnace at 300°C for 30 min. Volatile matter is eliminated during pyrolysis resulting in a carbon rich char (Cg as synthesized).

Figure 1. The plant *Calotropis gigantea* with stems, leaves, flowers and seeds.

The char is ground and sieved through 200 mesh. The fine carbon powder (Cg as synthesized) is treated with NaOH (10 wt.% aqueous solution) to remove impurities like silica followed by washing with excess distilled water and drying in air oven at 120°C. The carbon sample is further treated with conc. HCl (to remove metallic impurities like Na, K, Ca, Mg and Fe) followed by washing with excess distilled water and drying the sample in an air oven at 120°C. The carbon material obtained after treatment with NaOH and HCl is designated as Cg base acid.

Activation of Carbon Material

Two types of activating agents, namely carbonate (K_2CO_3) and oxalate ($Na_2C_2O_4$), were employed. The carbon material obtained after treatment with base and acid (Cg base and acid) was subjected to activation. The process of activation involves mechanical grinding of the carbon sample and the activating agent in a mortar and pestle. The reaction mixture (carbon and activating agent) taken in an alumina boat is placed in a tubular furnace. Inert atmosphere (N_2) is maintained in the furnace during the process. The temperature of the furnace was raised to 800 °C and maintained at that temperature for 2 h. The temperature of the furnace is then lowered. The contents were brought out and treated again with conc. HCl to remove the metallic impurities present in the activated carbon which are formed because of the decomposition of K_2CO_3 and $Na_2C_2O_4$ which are used as activating agents. The wt./wt. % ratio of carbon char to the activating agent is varied from 1:1 to 1:5 to evaluate the optimum amount of activating agent required to obtain highest porosity value and the corresponding BET specific surface area value (S_{BET}) of the activated carbon material was tested. When the ratio of the char from the stems of *Calotropis gigantea* (Cg) and the activating agent (K_2CO_3) were to be 1, 2, 3 and 4, the sample is designated as Cg carbonate 1, Cg carbonate 2, Cg carbonate 3, Cg carbonate 4, and Cg carbonate 5. Likewise, when the ratio of the char from the stems of *Calotropis gigantea* (Cg) and the activating agent ($Na_2C_2O_4$) were to be 1, 2, 3 and 4, the sample is designated as Cg oxalate 1, Cg carbonate 2, Cg oxalate 3, Cg oxalate 4, and Cg oxalate 5.

Characterization

SEM Analysis

SEM images of carbon materials were recorded using FEI QUANTA 200 FEG (virtual source) SEM equipped with an elemental analysis system. Carbon samples were mounted to aluminum stubs using carbon tape and loaded into the microscope under ambient conditions. As the carbon samples are conductive gold sputtering was not required.

C/H/N/S/O Analysis

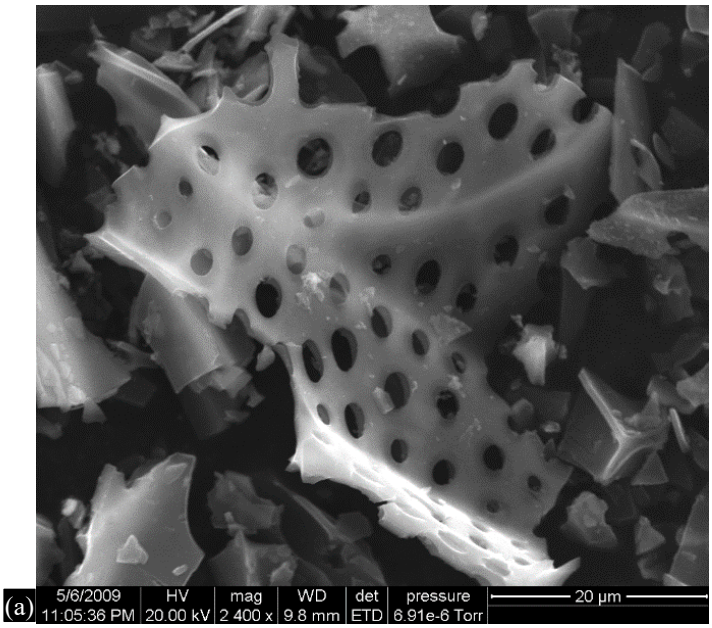
The elemental analysis of the carbon samples was carried out on CHNS/O analyzer (Perkin Elmer Instrument, Series II). Acetanilide was used as reference for calibrating the elemental analyzer. Prior to the analysis the samples were finely ground and dried in air oven at 120 °C overnight.

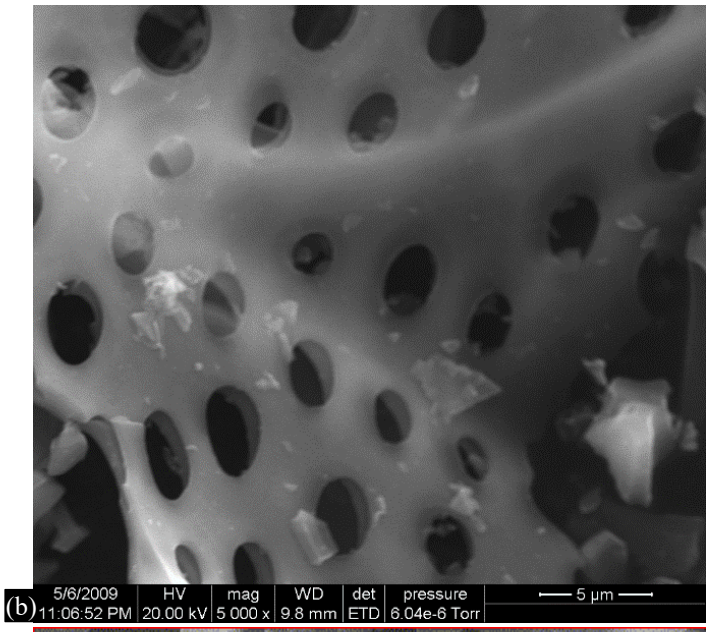
RESULTS AND DISCUSSION:

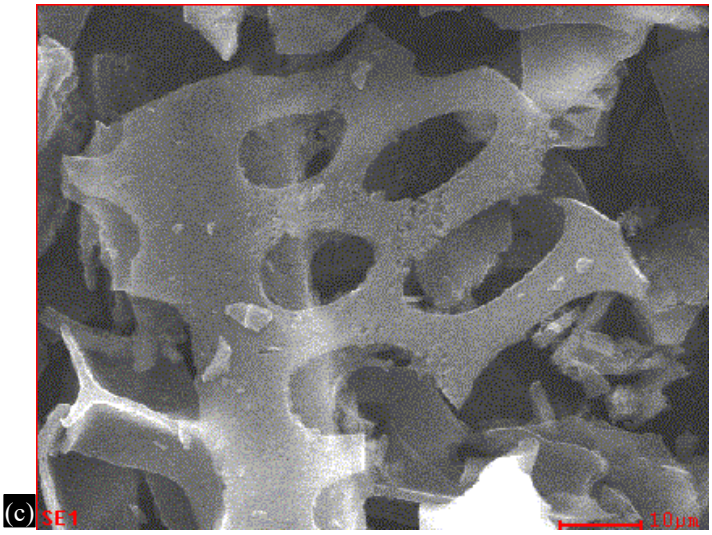
Effect of Activating Agent on the Morphology of Carbon Materials – Field Emission gun Scanning Electron Microscopy (FEG SEM) Analysis

Details of the surface morphology as well as the elemental composition of the activated carbon materials from *Calotropis gigantea* using carbonate and oxalate activation were obtained from (FEG-SEM) studies. The SEM images of carbonate activated carbon, designated as Cg carbonate 3 recorded at two different magnifications namely 2400 X and 5000 X were shown in Figure 2.

The Cg carbonate 3 possess a unique morphology. The carbon materials comprises of platelet like carbon particles with evenly distributed spherical pores. Such a morphology is unique to the carbon precursor, *calotropis gignatea* and has not been reported previously with any other lignocellulosic carbon precursor. The energy dispersive X-ray analysis indicated a carbon content of 92.62 wt.% and an oxygen content of 7.38 wt.% Unlike carbonate activation, oxalate activation resulted in a distinctly different carbon morphology. Activation with $Na_2C_2O_4$ resulted in a tubular morphology.







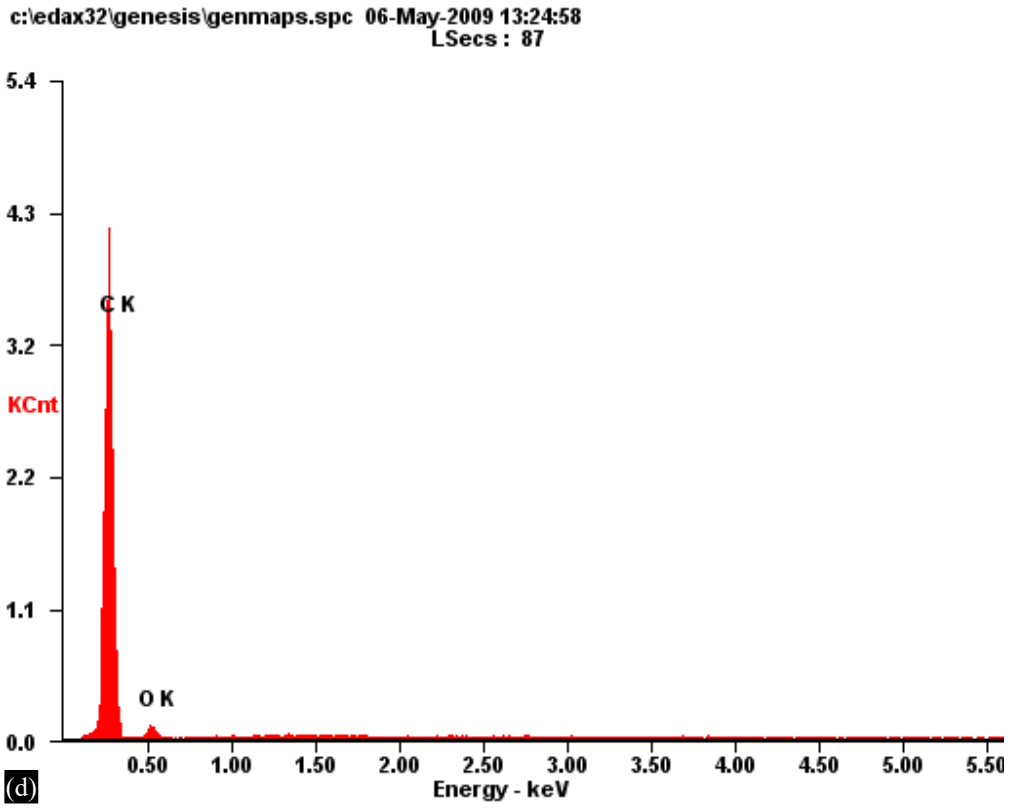


Figure 2. FEG SEM images (at different magnifications) of activated (carbonate) carbon material from *Calotropis gigantea*, Cg carbonate 3, along with energy dispersive X-ray analysis (EDXA) spectrum: (a) 2400 X , (b) 5000 X and (c & d) FEG SEM image with EDXA spectrum.

Bunches of carbon micro tubes with open ends were formed from the carbon precursor upon oxalate activation (Figure 2). At this stage it is surmised that the activators belonging to the organic groups (namely, oxalate, formate, tartate) work analogous to the physical activors like air [25].

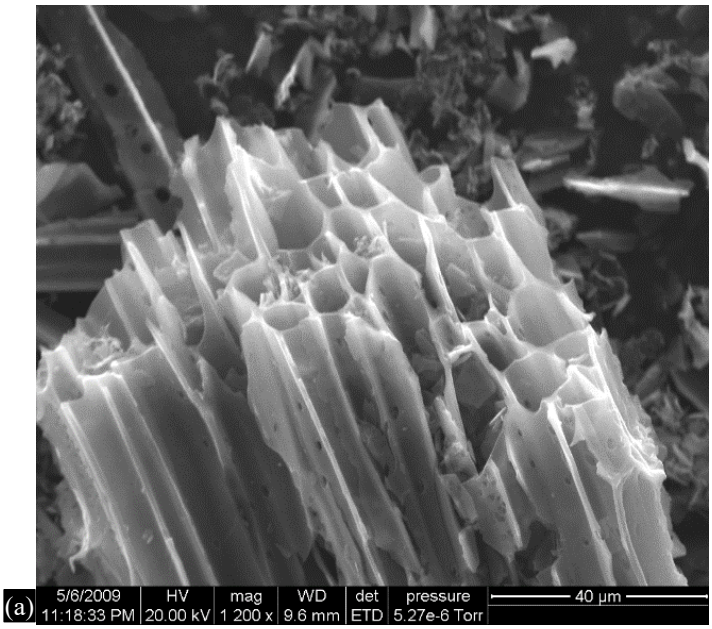
However, as such systems are seldom probed, molecular level mechanistic details are awaited. Energy dispersive X – ray analysis showed a carbon content of 92.49 wt. % and an oxygen content of 7.51 wt. %. Thus it is evident that the carbon morphology derivable is a function of the type of activating agent. Also the carbon precursor too dictates the morphologies achievable.

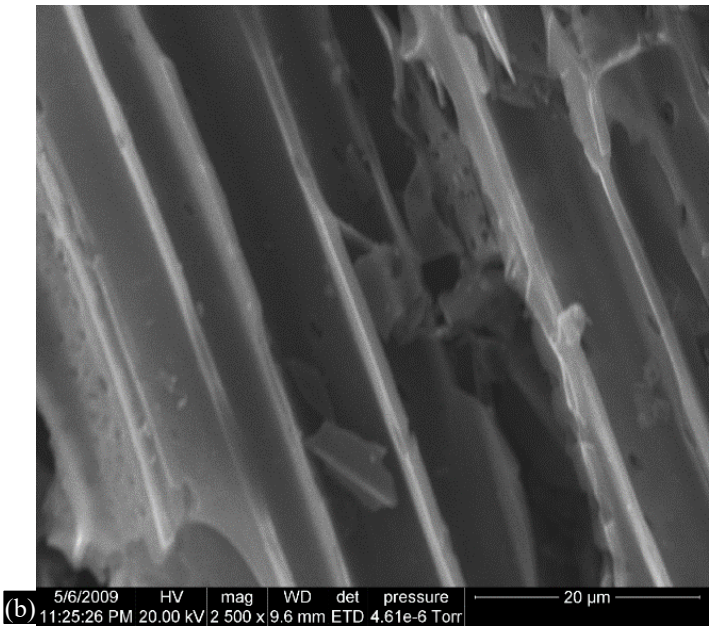
For comparison the surface morphology of commercially available activated carbon materials, namely, Black Pearl 2000, Vulcan XC 72 R and CDX 975 were recorded under. The SEM images recorded on the afore mentioned carbon materials at different magnifications are shown in Figure 3.

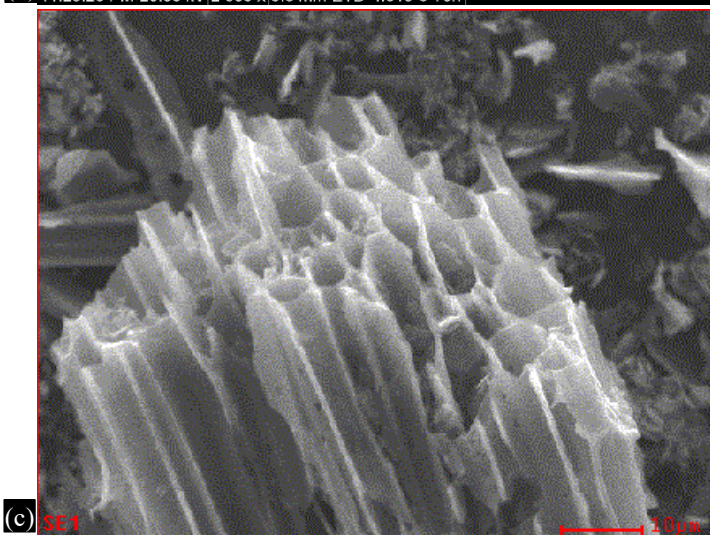
The carbon materials possessed spherical carbon nanoparticles. None of the commercial carbon samples examined offered the peculiar carbon morphologies derivable from the stems of *Calotropis gigantea* upon activation with carbonate and oxalate.

The commercial activated carbon materials too were analyzed by the energy dispersive X-ray analysis (EDXA) and the carbon and oxygen contents present in the carbon materials are summarized in Table 1.

For comparison, the elemental composition of the char and the base and acid treated char from the stems of Calogropis gigantea were shown in Table 2.







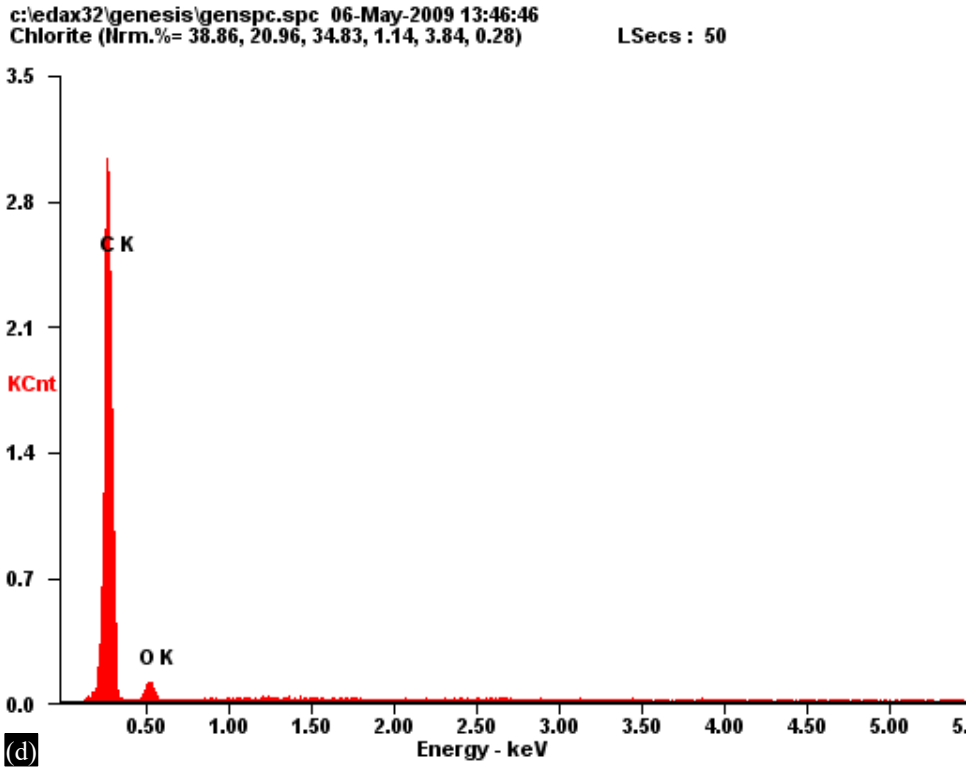


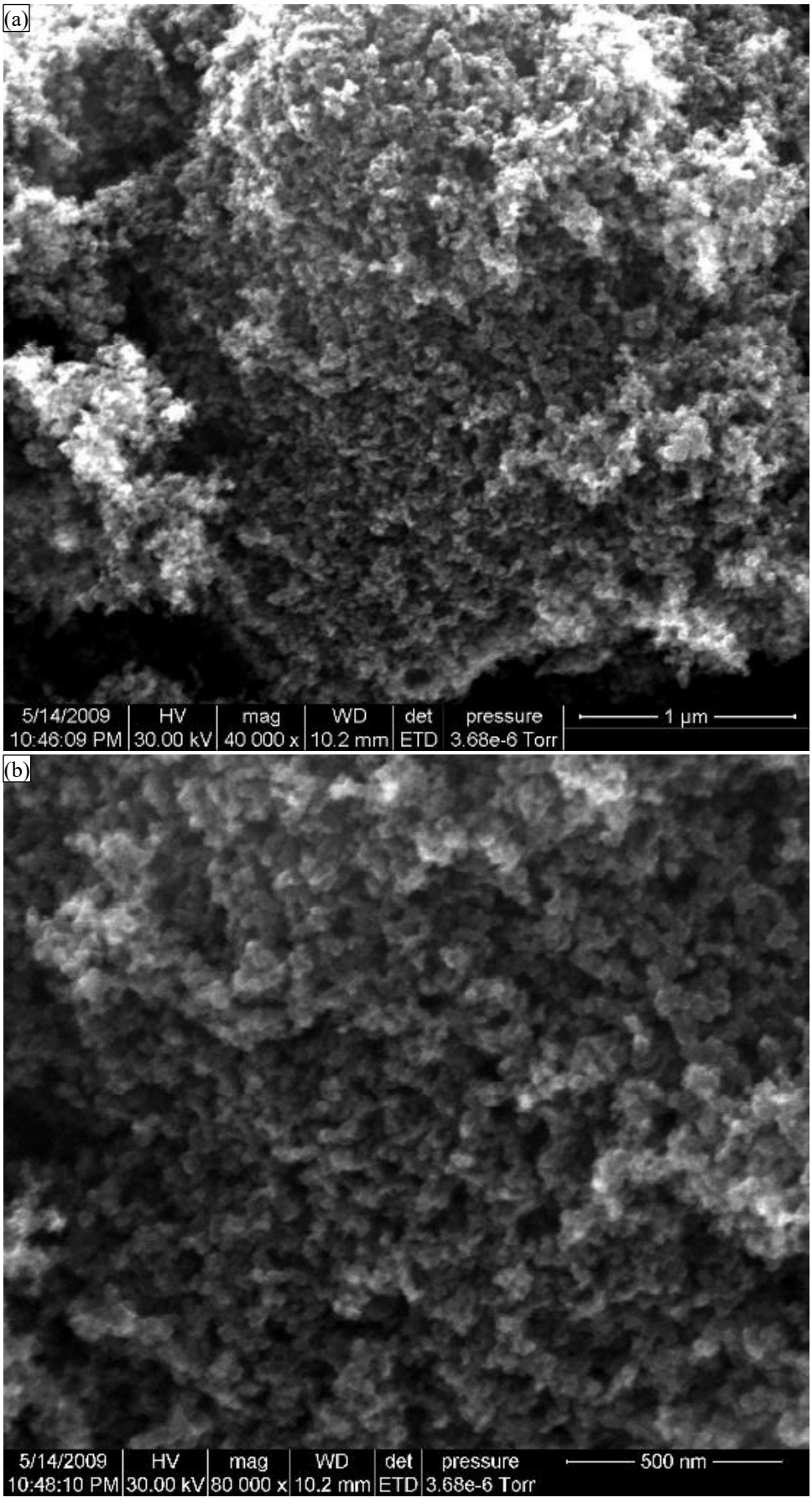
Figure 3. FEG SEM images (at different magnifications) of activated (oxalate) carbon material from *Calotropis gigantea*, Cg oxalate 4, along with energy dispersive X-ray analysis (EDXA) spectrum: (a) 1200 X (top view) (b) 2500 X (lateral view) and (c & d) FEG SEM image with EDXA spectrum.

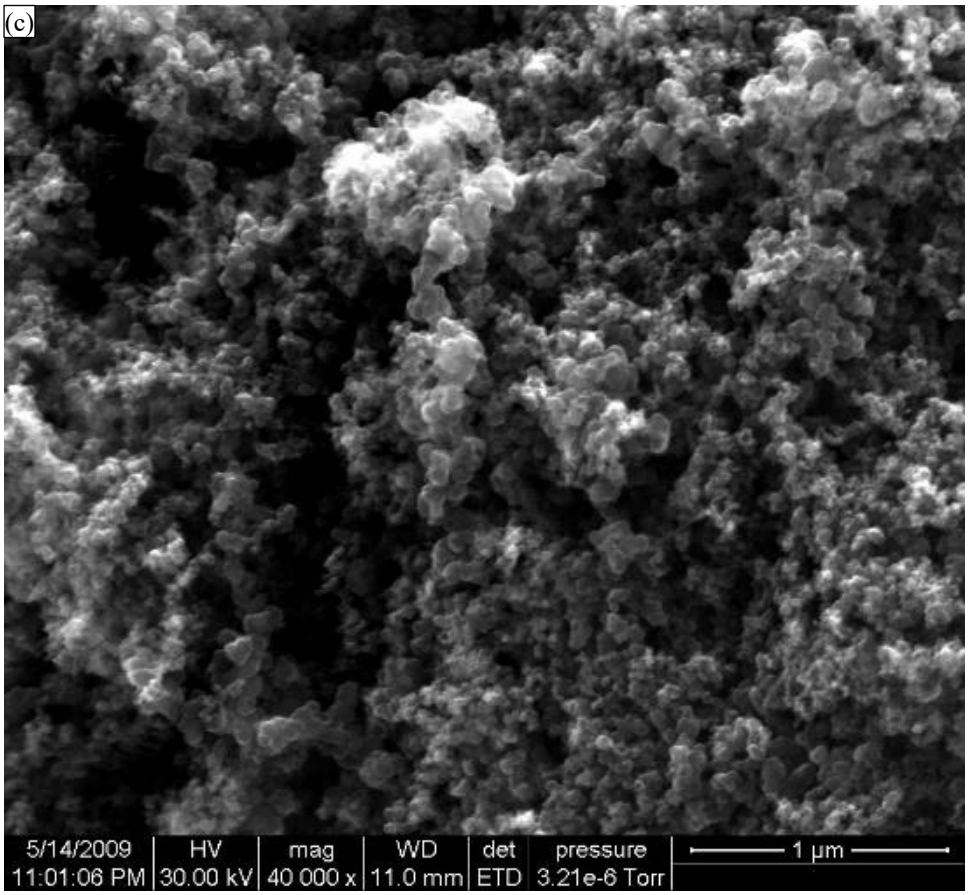
The carbon content of the plant based activated carbon materials produced through simple means is slightly lower than that of the of the commercial carbon materials owing to the surface enrichment of the activated carbon materials with oxygen functionality (as evident from the relatively higher amount of oxygen content of biobased activated carbon materials compared to the fossil based commercial activated carbon materials). A significant enhancement in the carbon content of the activated carbon material from *Calogropis gigantea* upon activation (~ 92 wt %) compared to either the char (~ 73 wt. %) or the char treated with the base (NaOH) followed by the acid (HCl) (~ 78 wt. %) was observed. Though, the morphology was significantly affected by the activating agent, there is almost no influence of the activating agent (either K_2CO_3 or $Na_2C_2O_4$) on the chemical compositon of the activated carbon materials.

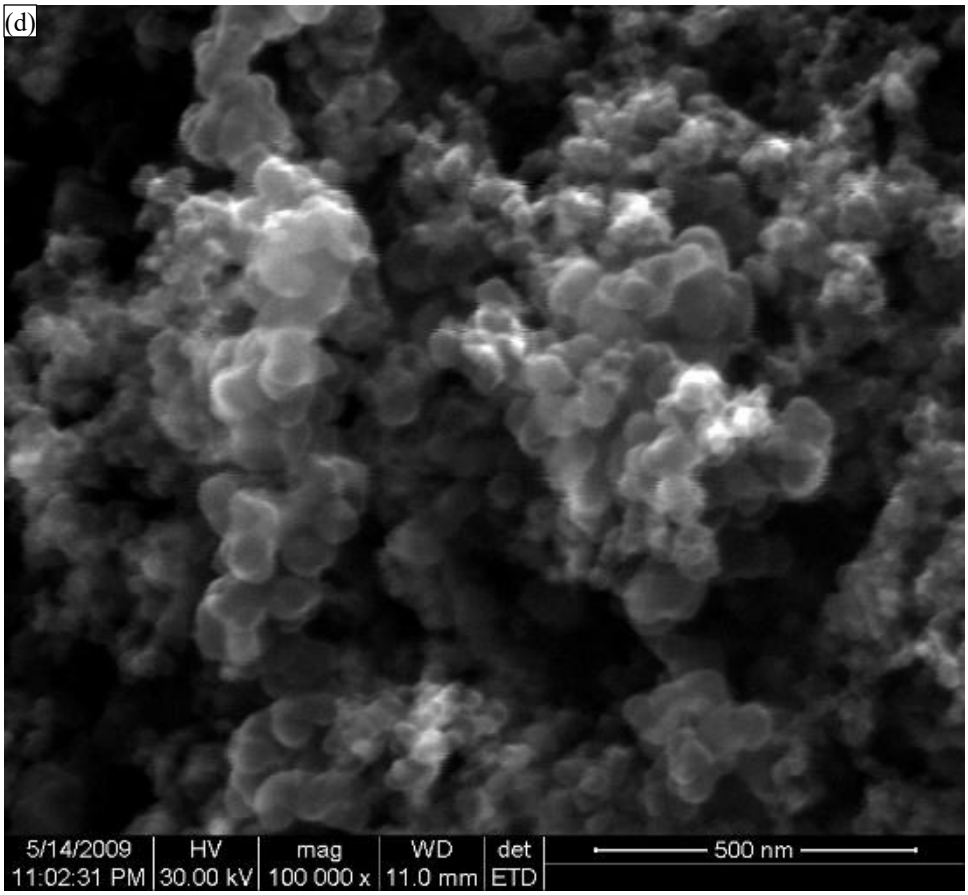
The different amounts of carbon and oxygent contents (wt. %) in the activated carbon materials, namely, Cg carbonate 3, Cg oxalate 4, shown in Table 1 and Table 2 are due to different methods, of analysis, namely, SEM with EDXA (Table 1) and C/H/N/S/O analyser (Table 2). Even though there appears to be a discrepancy, the values are as expected and are accurate owing to the fact the analytical measuring instrument, namely, SEM with EDX, quantifies the surface chemical composition, while the measuring instrument, C/H/N/S/O, gives the bulk chemical composition [26-30]. Thus the activating agents, whether inorganic or organic, do not effect the chemical composition (Tables 1 and 2), while they play a significant role in tailoring the surface morphology of the activated carbon materials (Figures 3 and 4).

Mechanism of Activation of the Char from *Calotropis gigantea* to Activated Carbon Material Using K_2CO_3 [13-17] and $Na_2C_2O_4$ [28-30] as Activating Agents

Even though the use of alkali metal hydroxides like KOH and NaOH as activating agents offer the advantage of producing carbon materials with high S_{BET} values, they (alkali metal hydroxides) are corrosive, hazardous and environmentally unfriendly.







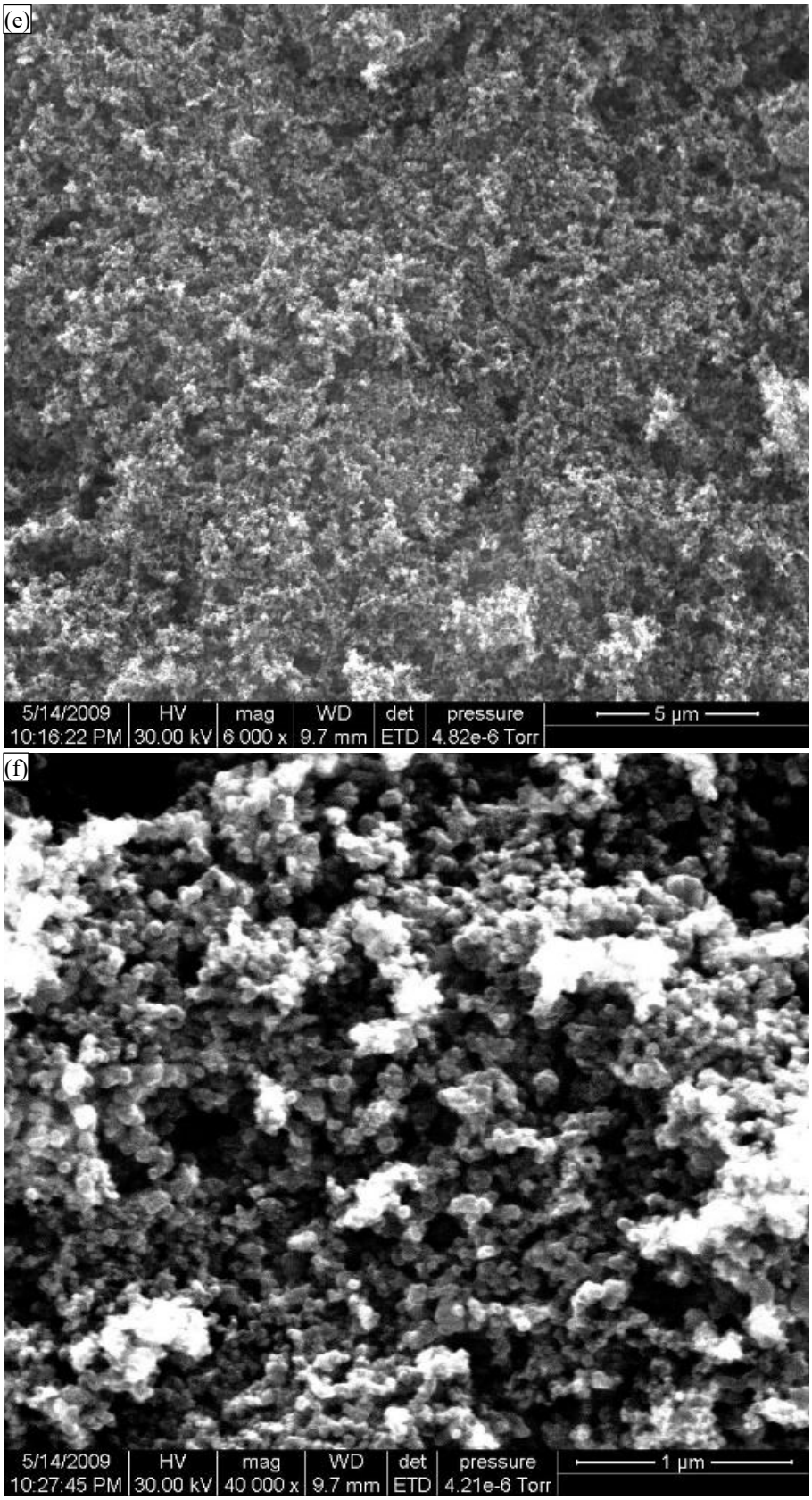


Figure 4. FEG SEM images (at different magnifications) of commercial activated carbon material: (a & b) Black Pearl 2000 (40, 000 X, 80, 000 X), (c & d) Vulcan XC 72 R (40, 000 X, 1,00, 000 X) and (e & f) CDX 975 (6000 X, 40, 000 X).

Table 1. Elemental analysis of activated carbon materials from the energy dispersive X-ray analysis (EDXA).

S. No.	Carbon Material	Element (wt. %)	
		Carbon (C)	*Oxygen (O)*
1	Cg carbonate 3	92.62	7.38
2	Cg oxalate 4	92.49	7.51
3	Black Pearl 2000	93.82	6.18
4	Vulcan XC 72 R	97.7	2.3
5	CDX 975	96.88	3.12

Table 2. Chemical composition of carbon materials from *Calotropis gigantean.*

Element (wt. %)	Carbon Materials from Calotropis gigantea		
	Cg as synthesized	*Cg base acid*	*Cg carbonate 3*
Carbon	73.13	77.62	80.04
Hydrogen	2.61	2.63	3.50
Nitrogen	0.81	0.82	0.67
Sulphur	0.36	0.33	0.36
Total	76.91	81.40	84.57
Ash content	12.7	4.0	1.8
Oxygen*	10.39	14.6	13.63

** By difference from the total amount of other constituents*

Use of alkali metal carbonates such as K_2CO_3 can be a substitute to the use of alkali metal hydroxides. K_2CO_3 was found to be a better activating agent owing to the formation of atomic K during the activation process (equation 1), which subsequently intercalates into the inter layers of adjacent hexagonal network plane of C atoms. The adjacent graphene planes were separated because of the K intercalation. Even after removal of K, either by washing with H_2O or acid, the rearranged or disordered graphene sheets of the carbon crystallite cannot go back to their original position thus leaving pores and voids. This results in an activated carbon material with high porosity and S_{BET} value [13].

Carbon reduces K_2CO_3 at elevated temperatures. As a result of the carbothermal reduction process (equation 1) potassium vapour and carbon monoxide are formed [14]. The occurrence of reaction (equation 1) is verified experimentally using Knudsen cell mass spectrometry. Potassium vapour and CO were detected in the gas phase during the reaction between carbon and K_2CO_3 in vacuum at temperatures in the range of 773–973 K.

$$2C + K_2CO_3 \rightarrow 2K + 3CO \quad (1)$$

Hayashi *et al*., have measured the weight loss rate behaviour of lignin as well as K_2CO_3 (activating agent) individually in N_2 atmosphere in the temperature range of 323 – 1273 K at a heating rate of 283 K/min [15]. Under identical conditions, the weight loss rate behaviour of lignin impregnated with K_2CO_3 is also measured and this is termed as experimental curve. In addition, the weight loss rate behaviour of lignin impregnated with K_2CO_3 is calculated by the summation of the values obtained from lignin and K_2CO_3 measured individually. The curve thus obtained was termed as calculated or theoretical curve. The assumption made in generating the calculated wt. loss rate curve is that there is no chemical interaction between the lignin and the activating agent. Thus the difference between the experimental and the calculated weight loss rate curves yield important insights into the chemical interaction as well as the particular weight losses resulting from the chemical reactivity between the char and the activating agent. It was noticed that the experimental weight loss peak at around 673 K shifted to a lower temperature in comparison to the peak position in the calculated or theoretical curve. Such a shift in the weight loss rate peak towards lower temperature (lower than 673 K) was attributed

to the occurrence of dehydrogenation reaction at a relatively low temperature. Such dehydrogenation reactions have not contributed to the enhancement of either S_{BET} or Vp but only indicate that the carbonization behaviour of lignin is altered or influenced by K_2CO_3 below 773 K. Also no convincing path way for the evolution of H_2 during activation in the presence of K_2CO_3 at such a low temperature (between 473-773 K) is illustrated.

Carbon materials are known to dehydrogenate evolving H_2 in the presence of alkali metals (Li, Na, K, Rb, Cs) at low temperatures [16, 17]. But the important question is that how H_2 evolution can take place in the presence of K_2CO_3 as activating agent under the reaction conditions where there is no possibility for the formation of alkali metal species. The following sequence of reactions offer a convincing pathway for the evolution of H_2 responsible for the observed weight loss rate peak at lower activation temperature (< 673 K) in the presence of K_2CO_3 as activating agent. K_2CO_3 is known to undergo thermal decomposition at a lower temperature in the presence of carbon char as shown in (equation 2).

$$K_2CO_3 \rightleftharpoons K_2O + CO_2 \tag{2}$$

The K_2O formed in (8) reacts with the structural or crystalline water evolved in the temperature range of 473 – 623 K from the carbonization mixture to form KOH (12).

$$K_2O + H_2O \rightarrow KOH \tag{3}$$

KOH thus formed in (equation 3) reacts with CO_2 formed in (equation 2) as well as with the carbon in the char to evolve H_2 as shown in (equation 4). The reaction, shown in equation 4, is thermodynamically feasible at a temperature as low as 673 K.

$$4KOH + CO_2 + \rightarrow 2K_2CO_3 + 2H_2 \tag{4}$$

In addition to the shift of the weight loss rate peak at a activation temperature of ≈ 673 K to a lower temperature, a huge difference in the weight loss rate behaviour is observed between the experimental and calculated curves at around 1073 K. In fact, a large peak (weight loss rate) is observed experimentally in sharp contrast to the theoretical or calculated curve where no weight loss rate peak was present. The observed weight loss rate was attributed to the release of CO by the carbothermal reduction of K_2CO_3 by carbon. Thus, K_2CO_3 acted differently in two different activation temperature ranges. Below an activation temperature of 773 K, K_2CO_3 acted as dehydrogenation agent and at an activation temperature of about 873 K, K_2CO_3 was reduced by C releasing CO and thereby increasing the S_{BET} and Vp values. Viet et al., provided insight into the mechanistic aspects of the generation of porosity using the activator, namely, $K_2C_2O_4$. The mechanism involves the insitu formation of the K_2CO_3 from the decomposition of $K_2C_2O_4$, with the rest of the steps being analogues to those shown in equations 1-4 [28-30].

CONCLUSION

The possibility of fine tuning the morphology of the activated carbon materials at the nanoscale as a function of nature (inorganic vs organic) and type of the activating agent is illustrated by considering the specific example of *Calotropis gigantea* stems as carbon precursor. Peculiar surface morphologies, unique to the carbon precursor, are generated simply by changing the activating agent (either carbonate or oxalate). Unusual, and exotic graphene line activated carbon material, with single layer thickness and uniform porosity, is obtained from activation with K_2CO_3. In contrast, a tubular morphology of the activated carbon material can be generated with $Na_2C_2O_4$ (sodium oxalate). A molecular level insight into the mechanism of activation using two different classes of activating agents, namely, carbonate and oxalate is presented. Obviously, the applications and ultimate performance of the activated carbon materials are dependent on the morphology, though such a morphology-function relation need to be

established beyond doubt. The sphere of usefulness of carbon materials is expected to increase manifold with the potential of activation recipes to provide a handle for fine tuning of the morphological features of carbon materials. So as to generalize the observation that inorganic and organic based activating agents result in strikingly different morphology from the same carbon biobased feedstock further experimentation on the morphology of the carbon materials with a series of inorganic and organic activating agents need to be systematically carried out and the underlying mechanism of activation need to be followed.

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