Ultrahigh Surface Area Carbon from Carbonated Beverages: Combining Self-Templating Process and in-situ Activation

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Abstract

Ultrahigh surface area carbons (USACs, e.g., $>2000 \text{ m}^2/\text{g}$) are attracting tremendous attention due to their outstanding performance in energy-related applications. The state-of-art approaches to USACs involve templating or activation methods and all these techniques show certain drawbacks. In this work, a series of USACs with specific surface areas up to $3633 \text{ m}^2/\text{g}$ were prepared in two steps: hydrothermal carbonization ($200 \text{ }^\circ\text{C}$) of carbonated beverages (CBs) and further thermal treatment in nitrogen ($600\text{--}1000 \text{ }^\circ\text{C}$). The rich inner porosity is formed by a self-templated process during which acids and polyelectrolyte sodium salts in the beverage formulas make some contribution. This strategy covers various CBs such as *Coca Cola*®, *Pepsi Cola*®, *Dr Pepper*®, and *Fanta*® and it enables an acceptable product yield (Based on sugars), for example: 21 wt% for carbon ($2940 \text{ m}^2/\text{g}$) from *Coca Cola*®. Being potential electrode materials for supercapacitors, those carbon materials possessed a good specific capacitance ($57.2\text{--}185.7 \text{ F g}^{-1}$) even at a scan rate of 1000 mV s^{-1} . Thus, a simple and efficient strategy to USACs has been presented.

1. Introduction

Nowadays, porous carbon materials have been applied in various fields, such as supercapacitor electrodes, catalyst supports, and gas sorbents, owing to their typically large surface areas.¹⁻⁹ Generally, activated carbons—the most popular commercial carbons—are prepared from the carbonization of biomass resources such as coconut shell; further oxidative etching activations such as exposure in harsh oxidizing atmospheres (e.g., CO₂, steam). In these processes, chemical treatments with acids (e.g., phosphoric acid), bases (e.g., KOH, NaOH), or salts (e.g., ZnCl₂, SnCl₂), are frequently used for directing porosities and increasing surface areas.¹⁰⁻¹⁴ For example, Fuertes and Sevilla *et al* prepared porous carbon adsorbents (2700 m²/g) by KOH activation of hydrochar from cellulose.¹⁵⁻¹⁶ In addition, salt melt synthesis is another powerful strategy for the chemistry of porous carbon materials. For instance, Antonietti and co-workers reported a series of highly porous carbons by the salt melt activation of different monomers, such as glucose (3200 m²/g), 1,4-dicyanobenzene (3300 m²/g) and ionic liquids (2000 m²/g).¹⁷⁻¹⁹ Meanwhile, carbon materials with well-defined mesopores (e.g., large pore channel, tunable pore structure, uniform pore size) were recently prepared by hard or soft-templating techniques, and those outstanding characters made them ideal candidates in specific fields.²⁰⁻³⁴ For instance, our group has synthesized mesoporous nitrogen-doped carbon (2121 m²/g) for oxygen reduction reaction by the combination of F127-mediated soft templating approach and ammonia activation.³⁵ However, a few issues related to processing and environment still remain in nanocasting methods. Indirect impregnation techniques require specific silica (e.g., silica colloidal spheres, silica colloidal crystals, ordered mesoporous silicas) as a template and the removal of silica by highly toxic hydrogen fluoride.²⁰⁻²⁶ Direct organic–organic self-assembly of triblock-copolymers and phenolic resins (phenol/formaldehyde) is presumably full of hope, yet restricted to distinct monomer families, though a few biomass-derived monomers/templates have been recently developed.^{27-34,36-39}

Approaches of combining different activation and templating methods were also reported for the synthesis of highly porous carbons. For example, Hu *et al* showed the synthesis of pistachio shell-derived carbons by a combination of KOH and CO₂ activation, and the resulting carbons held Brunauer–

Emmett–Teller (BET) surface areas up to 2145 m²/g.⁴⁰ Certainly, the specific surface area of carbon is an important factor, controlling its performance; for carbon chemists, it seems a great target to synthesize ultrahigh surface area carbons (USACs, e.g., >2000 m²/g). Even with above activation or templating strategies, USACs have been achieved only in a few cases, for example, carbide-derived carbons (3116 m²/g), zeolite-templated carbons (4100 m²/g) and chemically activated carbons from Spanish anthracite (3800 m²/g) or biomass rice hull (3960 m²/g).⁴¹⁻⁴⁹

In this contribution, we demonstrated the use of carbonated beverages (CBs) for a direct synthesis of USACs (S_{BET} up to 3633 m²/g) via hydrothermal carbonization (200 °C) together with thermal treatment (600-1000°C) in N₂ atmosphere (**Figure 1**). Typically, CBs have a high sugar content, i.e., around 110-130 g/L for most and these sugars are mainly in the form of glucose, fructose and sucrose, based on their formulas.⁵⁰⁻⁵¹ In addition, those additives in CBs such as phosphoric acids and polyelectrolytes are interesting, since previous works already suggested their porosity-directing role during the synthesis of carbon materials.⁵²⁻⁵⁴ A one-step process to porous carbons may be fabricated by hydrothermal carbonization (HTC) of CBs, if the CB's sugars are treated as the carbon precursor.

Figure 1. A general route to porous carbon materials from *Coca Cola*®.

HTC is actually an old process that can be described as the artificial acceleration of carbohydrate decomposition and polymerization under low temperature and self-generated pressure. Recent studies on carbon materials once again highlight the good performance of HTC in the feasible transformation of

sugar-based systems, such as: glucose, fructose, cellulose and raw biomass.⁵⁵⁻⁶¹ Besides being fast and easy-to-handle, HTC inherently tolerates wet starting stocks and CBs could be directly processed without any pretreatment, since effective dehydration proceeds just in the presence of water. Moreover, the final carbon product can be separated from the reaction mixture by a simple filtration and complicated isolation procedures can in principle be avoided. Based on all the advantages mentioned above, it is promising to transform CBs into useful USACs by HTC.

2. Experimental Section

2.1 Carbon Preparation

Soft drinks including *Coca Cola* ®(13 wt% sugars), *Pepsi Cola* ®(13 wt% sugars), *Dr Pepper* ®(13 wt% sugars), and *Fanta* ®(15 wt% sugars) were used as the starting materials. Typically, 30 mL of the soft drink was loaded into a PTFE-lined autoclave and heated at 200°C for 24 hours in an oven under air. The resulted mixture was then thoroughly washed with 500 mL deionized water and 500 mL ethanol, and filtrated to yield dark red solids. Part of those materials were further post-carbonized at 600/800/1000 °C (heating rate: 10 K/min, holding time: 2 h) under an inert N₂ atmosphere (200 mL/min) to yield the black carbon materials.

2.2 Physical Characterizations

SEM and TEM characterizations were performed using a Hitachi HD-2000 operating in STEM mode using a secondary electron (SE) and/or bright-field STEM detector operating at 200 kV. To prepare samples for electron microscopy analyse, the as-prepared materials were dispersed in ethanol using an ultrasonic bath to yield fine suspensions, which were transferred to lacy carbon-coated 200-mesh copper TEM grids and dried in ambient air. Nitrogen adsorption isotherms were measured at –196°C using a TriStar 3000 volumetric adsorption analyzer manufactured by Micromeritics Instrument Corp. (Norcross, GA). Before adsorption measurements, samples were degassed in flowing argon at 150°C overnight. The specific surface area of the samples was calculated using the Brunauer-Emmett-Teller (BET) method within the relative pressure range of 0.05 to 0.20. Pore size distributions were calculated

using the Barrett-Joyner-Halenda (BJH) model. The total pore volume was determined from the amount of N₂ uptake at a relative pressure of $P/P_0 = \sim 0.95$. X-ray diffraction patterns were recorded on a Siemens D5005 diffractionmeter with Ni-filtered Cu K α radiation operating at 40 kV and 40 mA.

2.3 Electrochemical Characterizations

For the electrochemical measurement, 5.0 mg of the as-prepared material, 1.0 mg of onion-like carbon (From Yury Gogosti Group),⁴⁹ and 7.5 μ l 5 wt% Nafion solution were first mixed in 1.0 ml of isopropanol, and dropcasted on a well-polished glassy carbon electrode to yield a loading of $\sim 500 \mu\text{g cm}^{-2}$. Cyclic voltammetries (CVs) were carried out in 6.0 M KOH from -1.0 to 0 V vs. Hg/HgO at different scan rates. The specific capacitance (C_g) was calculated from the CV curve following the formula:

$$C_{sp} = \frac{\int i(E)dE}{2\Delta E m \nu}$$

where C_{sp} is the specific capacitance of individual sample. $i(E)$ is the instantaneous current, $\int i(E)dE$ the total voltammetric charge obtained by integration of positive and negative polarizations in a cyclic voltammogram, ΔE is the potential window width, m is the mass of the sample in the electrode, and ν is the scan rate.

3. Results and Discussion

Coca Cola® with 13 wt% sugar was first selected as a model of CBs. 30 ml of *Coca Cola*® drink was loaded into a Teflon lined autoclave and the reactor was treated at 200 °C for 24 hours. Around 1.6 g of dark red powder was obtained after washing the resulting mixture with water and ethanol. Product yield, respecting to sugars in the starting drinks, could reach 41 wt% (**Table 1**), which is close to that by HTC of pure glucose (32-38 wt%).⁶²⁻⁶³ The weight loss is possibly due to the sugar dehydration under HTC conditions. The HTC material was further carbonized at temperatures from 600 to 1000 °C under an inert N₂ atmosphere to yield the corresponding carbon material. These final carbon materials were denoted as C-600, etc.; where the first character directs to the soft drinks (C: *Coca Cola*®, P: *Pepsi Cola*®, D: *Dr Pepper*®, F: *Fanta*®), while the last number ‘600’ means the final treated temperature. The process

could afford an acceptable product yield (up to 21 wt%) even though primary HTC materials were treated at 1000 °C (Table 1).

Table 1. Characterization of carbon materials from carbonated beverages.

Sample	Yield (g) ^a	Yield (g) ^b	S _{BET} (m ² g ⁻¹) ^c	Pore Volume (cm ³ g ⁻¹)	APS (nm) ^d
C-200	41	53	8	-	-
C-600	25	33	554	0.27	1.9
C-800	24	31	828	0.38	1.8
C-1000	21	27	2940	2.01	2.6
P-200	31	40	9	-	-
P-600	18	23	508	0.24	1.7
P-800	17	22	799	0.34	1.8
P-1000	15	20	2687	1.27	1.8
D-200	30	39	10	-	-
D-600	17	22	792	0.26	1.8
D-800	15	20	933	0.43	1.7
D-1000	13	17	1539	0.72	1.8
F-200	31	35	1	-	-
F-600	19	25	510	0.23	1.6
F-800	15	20	1026	0.61	1.8
F-1000	9	12	3633	1.63	1.8

^a Yield per 100 grams of sugars. ^b Yield per liter of carbonated beverage. ^c Specific surface area calculated using the Brunauer-Emmett-Teller (BET) method for the adsorption data in the relative pressure interval from 0.05 to 0.20. ^d APS: average pore size from Barrett-Joyner-Halenda (BJH) adsorption curves.

In comparison with pure glucose/fructose (C: 40.0 wt%), a significant increase of carbon content (64.2 wt%) was observed in C-200 sample and the carbon content of C-1000 sample could reach 86.3 wt%, confirming the “carbonization effect” (**Figure 2a**). Elemental analysis illustrated that heteroatoms such nitrogen and sulfur were also incorporated in the carbon materials, which may be induced by the co-polymerization of sugars with additives (Figures S1-S2). The FTIR spectra indicate that the increase of carbonization temperature will lead to the continuous release of active groups (e.g., -OH group) and structural rearrangement and leave the sp² bonded carbon backbone finally (**Figure 2b**). The C-200 sample is typical of disordered glassy polymer without pronounced order, as suggested by the wide humps in the X-ray diffraction (XRD) pattern. All the carbon materials afforded a broad reflection around 25° and a weak reflection around 44° in XRD patterns, which could be attributed to the (002) and

(100) reflection of the graphitic-type lattice; therefore these carbon materials hold amorphous structures (Figure 2c).

Figure 2. a) Carbon content, b) FTIR spectra and c) XRD data of Carbons from *Coca Cola*[®].

Figure 3 shows typical scanning electron microscope (SEM) and transmission electron microscopy (TEM) images of the as-prepared carbon materials. The C-200 sample is composed of rough carbon spheres with the diameter in the range of 300-400 nm, which are further interconnected to form a grape vine-like network (Figure 3a-3c). Note that direct HTC of glucose also results in carbonaceous particles that are similar with those observed here.⁶³⁻⁶⁴ Based on above observations, the HTC of CBs may undergo a typical sugar decomposition pathway. Initially, the carbohydrate decomposes into hydroxymethylfurfural (HMF) which goes through a polymerization–polycondensation process to form

small nuclei. These nuclei grow according to a LaMer model until all the “monomers” have been consumed and the final carbon particle is attained.⁵⁶⁻⁵⁷ After thermal treatment of primary HTC carbons in N₂, interesting porosity inside the carbon units were generated. For example, the C-1000 material was rich in apparent micropores throughout the whole nano-architecture (**Figure 3e-3f**).

Figure 3. a) and b) SEM images of C-200, c) TEM image of C-200, d) TEM image of C-600, e) and f) TEM images of C-1000.

The N₂ sorption measurements were then carried out for the carbons derived from CBs (**Table 1**). The sorption isotherm of C-200 illustrates negligible N₂ uptake (data not shown, 8 m²/g), indicating the

absence of porosity that is usually observed for HTC carbon materials.⁶³⁻⁶⁴ In sharp contrast, samples after high temperature calcination (600, 800 and 1000 °C) clearly presented higher N₂ uptakes, which is in agree with the observation of inner porosity in above TEM images (**Figure 4a**). The isotherm curves of C-600 and C-800 can be assigned to type I with significant sorption at a low relative pressure, and C-600 and C-800 are typically microporous carbons with BET surface areas of 554 and 828 m²/g, respectively. Interestingly, a much higher N₂ uptake was observed in the case of C-1000 sample, and the N₂ sorption behaviour was, more or less between type I and type II, i.e. it features a mixture of high N₂ uptake at P/P₀<0.05 with continually increasing absorption at higher P/P₀ (0.05–0.5) for developed mesopores (**Figure 4b**). The mesoporous channel may be induced via the re-structure of the carbon backbone during high tempeature treatment. The BET surface area of C-1000 was found to be 2940 m²/g. It should be outlined that no other templates, additives or activating agents are intentionally added for this process. As C-1000 presents a high total pore volume (2.01 cm³/g at P/P₀ = ~ 0.95), it may provide a vast domain for electrolyte transfer and exposing reactive sites.

Encouraged by interesting results above, several other soft drinks such as *Pepsi Cola*®, *Dr Pepper*® and *Fanta*®, were then examined under the HTC process. Those HTC carbons (P-200, D-200 and F-200) were obtained in good yields (31 wt%, 30 wt% and 31 wt%, respectively). Once again, thermal treatment (600-1000 °C) in N₂ atmosphere was effective for constructing porous carbons, and 1000 °C was a optimized temperature for specific surface area. It is interesting that for the carbon samples, the increase of thermal treatment temperature from 800 to 1000 °C leads to a significant increase on the specific surface area, while the product yield only decreases slightly (Table 1). A catalytic reaction by the additives may occur during the thermal treatment. Among microporous carbons from different precursors, the F-1000 sample gave a high specific surface area of 3633 m²/g, while P-1000 and D-1000 showed values of 2687 m²/g and 1539 m²/g, respectively (**Figure 4c, 4d**). Therefore, it is reasonable to consider that a general and useful process to highly porous carbon, respecting to the specific surface area, has been established.

Figure 4. a) N₂ sorption isotherm curves of C-600, C-800 and C-1000, b) Pore size distribution of C-1000, c) and d) N₂ sorption isotherm curves for P-1000, D-1000 and F-1000 samples.

Current synthesis of CBs-derived carbon might be a self-templated process, since thermal treatment of sugar alone would only lead to carbon material with low porosity. For example, Antonietti, Titirici and Wang showed that the carbons from HTC of glucose/fructose with further thermal treatment in N₂ possessed relatively low specific surface areas.⁶³⁻⁶⁴ We would further probe the reason that controls the porosity of CBWs-derived carbons. Among those main formulas in soft drinks,⁶⁵ sugars (glucose, fructose and sucrose) could serve as carbon sources via a dehydration-polymerization-polycondensation process, while the condensed CO₂, acids (citric acid or H₃PO₄) or polyelectrolyte sodium salt may be possible species that are contributing to the porosity. The pore creating effects of those compounds have already been suggested in previous systems, and a series

of controlled experiments were then carried out. A careful HTC of *Coca Cola*® without any CO₂ (Fresh drink was open for three days) confirmed that the incorporated CO₂ do not affect this process, as the corresponding sample held a similar BET surface area (2940 vs 2734 m²/g; with or without CO₂, respectively). A initial test showed that the pH value of *Coca Cola*® is ~2 and we would then move toward the effect of acids on the HTC process with glucose as an example. Controlled HTC of glucose with H₃PO₄ or citric acid additives were then carried out, followed by thermal treatment at 1000 °C (Labeled as G-P-1000, G-C-1000, **Figure 5**, **Figure S1**). The G-P-1000 and G-C-1000 samples showed BET surface areas of 459 and 396 m²/g with microporous character, higher than the value (285 m²/g) from blank sample. Controlled processes with polyelectrolyte sodium salts (kayexalate or sodium polyacrylate) also afforded increased surface areas, in accordance with recent works by Wang group.⁶⁶⁻⁶⁷ Hence, we conclude that acid or sodium salt additives in soft drinks may play a role in directing porosity upon further carbonization. Since most additives in the soft drinks have been protected and patented, we, at current stage, cannot go to a detailed analysis. Future works on the mechanism study will be expected to perform in cooperation with the soft drink company. In this work, we are focusing on the processing of CBs into porous carbons and subsequent applications.

Figure 5. Specific surface areas for carbons *via* HTC of glucose in the presence of different additives.

Reaction condition: 3.9 g glucose, 1 g additive, 30 mL H₂O; 180 C for 24 h and 1000 C for 2 h.

Recently, carbon-based supercapacitors have gained more and more attention, among which the surface area and pore size of carbon electrodes are considered as key factors affecting their performance.⁶⁸⁻⁷¹ Given that CBs-derived carbon materials possess high specific surface area—available for the electrostatic adsorption of electrolyte ions, we would subsequently perform electrochemical tests of F-1000 and C-1000 (**Figure 6**). The cyclic voltammetry curve of F-1000 in a basic media (6 M KOH) demonstrated the rectangular shape at a sweep rate of 5-100 mV s⁻¹, a typical double-layer capacitance behavior and the corresponding specific capacitances were 186-144 F g⁻¹. The specific capacitance of this material decreased to 115 F g⁻¹ as the scan rate increased to 1000 mV s⁻¹, and a relative capacitance of 62% remains, in comparison with the value under 5 mV s⁻¹. Such phenomena actually is common for microporous carbons and possibly originates from the insufficient time available for ion diffusion and adsorption inside smaller pores. Meanwhile, the distortion of CV curves at higher sweep rates (600 and 1000 mV s⁻¹) revealed that diffusion seems to limit the ion adsorption on the electrode surface in some degree. It is reasonable since this F-1000 material was actually dominated by micropores. In addition, the C-1000 sample held a specific capacitance of 149 F g⁻¹ at 5 mV s⁻¹ and a moderate capacitance of 76 F g⁻¹ was observed when the scan rate was increased to 1000 mV s⁻¹.

Figure 6. a) Cyclic voltammograms of F-1000 sample recorded at scan rates from 5 mV/s to 1000 mV/s; b) Evolution of the specific capacitance versus scan rate for F-1000 sample; c) Cyclic voltammograms of C-1000 sample recorded at scan rates from 5 mV/s to 1000 mV/s; b) Evolution of the specific capacitance versus scan rate for C-1000 sample.

4. Conclusions

In summary, we have illustrated the possibility of constructing USACs (up to 3633 m²/g) by a facile process with CBs as abundant carbon sources. This synthesis strategy was inspired by the HTC of biomass, however it afforded some unique features—It do not rely on any additional templates, additives or activations and those CBs-derived carbons showed ultrahigh surface areas. The essence of this self-templated synthesis lies in those active species in the beverage formulas, among which the acids/polyelectrolyte sodium salt might be potential compounds for directing porosity. Importantly, this method allows an acceptable product yield, for example: 27 grams C-1000 sample (2940 m²/g) can be obtained from per liter *Coca Cola*[®] (~130 grams sugars). This promising process provides an

exceptional route to highly porous carbon materials.

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