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Research Article

Heat Treatment of Buckypaper for Use in Volatile Organic Compounds Sampling

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Three types of buckypapers (BPs), two of them fabricated with arc discharge (AD) single-walled carbon nanotubes (SWNTs) (acetone-cleaned AD BP and methanol-cleaned AD BP) and one with high-pressure carbon monoxide (HiPco) SWNTs (HiPco BP), were heat-treated at different conditions to find the specific conditions for each type that improve the adsorption properties. Based on thermogravimetric analysis (TGA) data, three heat treatment conditions were designed for the AD BPs and another three conditions for the HiPco BPs. Also, changes in weight and physical integrity before and after the heat treatment were considered. Heating at 300°C for 90 minutes was selected for acetone-cleaned AD BP, in which the BP kept its physical integrity and yielded a relatively high Brunauer, Emmett, and Teller (BET) surface area ($970 \pm 18\ m^2/g$), while methanol-cleaned AD BP was excluded because of its physical change. For HiPco BP, a condition of 300°C heating for 30 minutes was chosen as a relatively higher surface area ($933 \pm 54\ m^2/g$) and less weight loss (5%) were observed.

1. Introduction

Strategies to fabricate CNT films or buckypaper (BP) have been developed mostly for use in electronic devices [1]. Processes such as vacuum filtration, solution spraying, drop casting, and layer by layer assembly have been widely investigated and successfully used [1, 2]. Certain fabrication methods such as vacuum filtration or solution spraying commonly require suspending CNTs in surfactants for obtaining a homogenous solution and, after the deposition on a substrate like a membrane filter or glass, rinsing the deposited cake with purified water to remove the surfactants [1, 3, 4]. Surfactants could insulate CNTs and possibly lower their conductivity [5, 6]. Although it is often thought that the surfactants could be completely removed with water rinsing [3, 7], studies have found remaining surfactants in SWNT films [5–7]. Additional purification process of surfactants such as heat or acid treatments has been suggested [5–7].

In our previous study for the application of the photothermal desorption (PTD) [8], arc discharge (AD) and high-pressure carbon monoxide (HiPco) single-walled carbon nanotubes (SWNTs) were fabricated into BPs through the vacuum filtration method, a relatively simple and inexpensive procedure [1, 6]. We determined that the fabrication process left surfactant residues in AD BPs. Since AD SWNTs were presuspended in surfactants (i.e., sodium cholate and sodium dodecyl sulfate) when purchased, a cleaning process with DI water and solvent rinsing was involved; however, increased weight of the BP compared with theoretically predicted weight was observed even after the cleaning, which was attributed to the residual surfactants left within the fabricated AD BPs.

The purpose of this study was to find the appropriate heat treatment conditions for each type of BP in order to improve adsorption properties by removing surfactants or solvent related impurities. For AD BPs, our main purpose was to remove surfactants imbedded in AD BP rather than removing metal impurities, so heat treatment at a mild temperature was performed. Because of the low probability for SWNTs to be oxidized at mild temperatures [6, 9, 10] and simplified furnace operation, heat treatment was performed in air environment. In addition, HiPco BPs were included in this study

mainly to remove any impurities involved in the synthesis and fabrication process. Thermogravimetric analysis (TGA) was performed in advance to determine appropriate heat treatment conditions specific to each type of BPs.

2. Materials and Methods

2.1. Buckypaper (BP) Fabrication. The fabrication procedure was adopted from our previous study [8]. Arc discharge (AD) SWNT solution (1 mg/mL, 94.5% pure, 1.2–1.7 nm in diameter, 0.1–4 μm in length) presuspended in surfactants (1% w/v sodium cholate and sodium dodecyl sulfate in water) and HiPco SWNTs (85% pure, 0.8–1.2 nm in diameter, 0.1–1 μm in length) powder were purchased from Nanointegris Inc. (Quebec, Canada). A typical filtration and suspension procedure to fabricate BPs was employed and two fabrication/cleaning methods for AD BP (i.e., acetone-cleaned and methanol-cleaned) and one method for HiPco BP were used. For the fabrication of AD BPs, 50 mL (50 mg) of the AD SWNT solution was mixed with 400 mL of solvent (either acetone or methanol) for 15 hours. The suspension was then vacuum-filtered through a polytetrafluoroethylene (PTFE) membrane filter (47 mm in diameter, 5 μm pore, EMD Millipore, Darmstadt, Germany) and a series of two alternating rinses were used after the SWNT cake was deposited on the filter but not dried. The SWNT cake was first rinsed with 250 mL of deionized water (18.2 MΩ cm) and then 50 mL of solvent to make either acetone-cleaned or methanol-cleaned AD BP. The deposited cake was allowed to dry for 30 minutes under vacuum plus another 2 hours without vacuum while on the membrane filter and a BP was obtained by delaminating the dried SWNT cake from the filter. For HiPco BP preparation, 50 mg of powdered HiPco SWNTs was suspended in 400 mL methanol and ultrasonicated using a 490 W bath sonicator (BRANSON CPX5800H, Danbury, CT) for 150 minutes. The solution was vacuum-filtered through the same type of PTFE membrane filter and allowed to dry in the same way as mentioned before (30 minutes under vacuum plus another 2 hours without vacuum). The SWNT cake was then delaminated from the filter to obtain a BP.

2.2. Thermogravimetric Analysis (TGA). TGA (Q500, TA Instruments, New Castle, DE) was performed on the fabricated BPs. Two BPs of each fabrication method were used and results were averaged. The samples were held at 120°C for 20 minutes to remove residual moisture and heated to 800°C with a ramping rate of 10°C/min in air environment, followed by 45-minute hold. Based on the data obtained (see Results), further heat treatment conditions were determined. For the AD BPs, three conditions were set in which the surfactants were expected to be completely removed without a considerable weight loss compared with the theoretically predicted weight (i.e., 50 mg): 300°C for 90 min, 350°C for 60 min, and 300°C for 120 min. For the HiPco BPs, the treatment conditions were set where the surface area was expected to be increased with a minimal weight loss: 350°C, 300°C, and 250°C for 30 min.

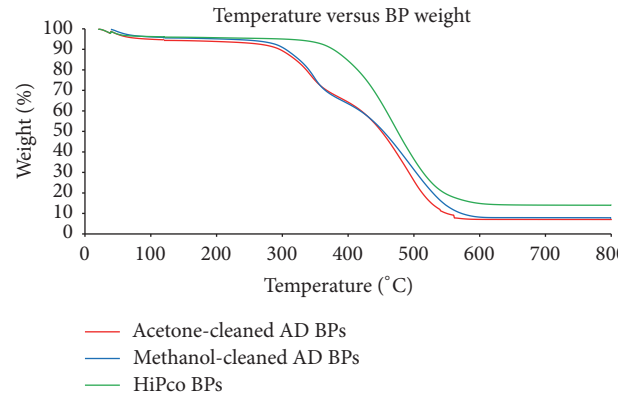


Figure 1: TGA results for acetone-cleaned AD BPs, methanol-cleaned AD BPs, and HiPco BPs.

2.3. Heat Treatment. Heat treatment was performed with a muffle furnace (Thermolyne™ F48025-60-80, Thermo Fisher Scientific™, Waltham, MA). The ramping rate was 10°C/min and samples were held for the designated conditions (time and temperature) and then cooled down to room temperature. Changes in weight and physical integrity (i.e., appearance and surface) were recorded before and after heat treatment.

2.4. Characterization of Adsorption Properties. Surface area and pore size were analyzed with a physisorption analyzer (Micromeritics® ASAP 2020, Norcross, GA) using N_2 at 77 K. Samples were degassed for an hour at a temperature in which each sample was heat-treated prior to the measurement. Analysis was duplicated for each BP and averaged. Brunauer, Emmett, and Teller (BET) theory was used to determine surface area and subsequently mean pore width.

3. Results and Discussions

3.1. TGA. 10% weight loss of acetone-cleaned AD, methanol-cleaned AD BPs, and HiPco BPs occurred at an average of 295 ± 9, 305 ± 0, and 377 ± 5°C, while 50% of weight loss occurred at 451 ± 3, 454 ± 1, and 474 ± 1°C, respectively (Figure 1). Since the weight of the fabricated AD BPs was higher (approximately 30%) than the theoretically predicted weight (i.e., 50 mg) because of the residual surfactants and only 10 mg of BP was used for TGA, the data was rescaled considering the original weight of the BPs (Figure 2). The temperature where the weight of AD BPs became 50 mg was recalculated considering the new scale and resulted in 381 and 362°C for acetone-cleaned and methanol-cleaned AD BPs, respectively. Both AD BPs showed a similar decomposition pattern as expected which led to the same conditions for the heat treatment.

The theoretically predicted weight of 50 mg is the amount we calculated from the SWNT suspension for AD BPs and the amount we weighted on a scale for the powder form HiPco SWNTs, which may result in variations between BP samples since measuring the exact same amount every time is not possible. We assumed that samples below the theoretical weight

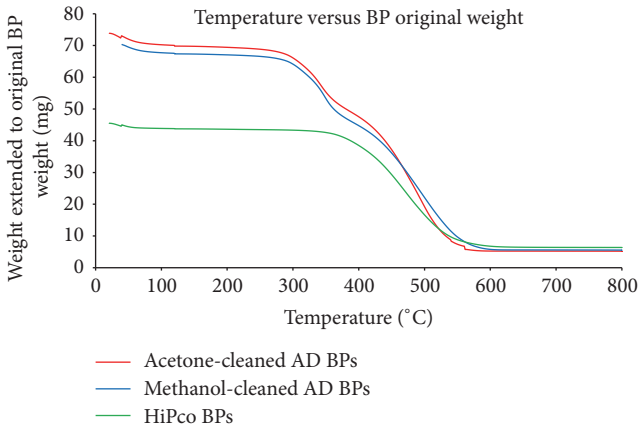


Figure 2: Rescaled TGA data.

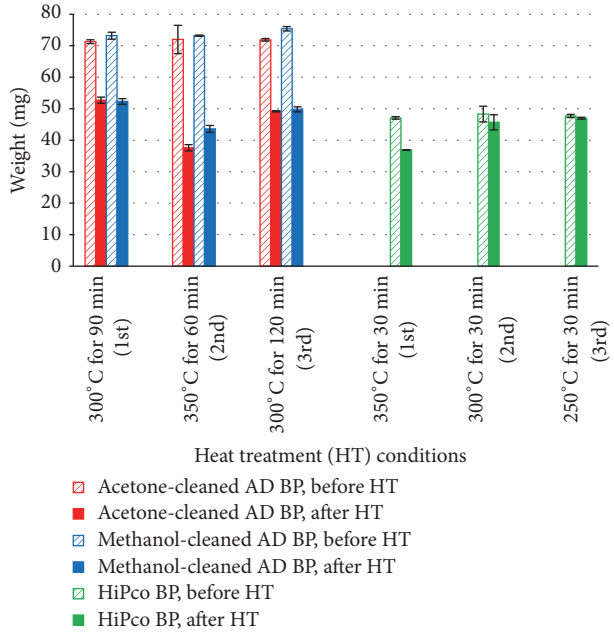


Figure 3: Weight change before and after heat treatment.

will only contain the pure material and surfactants/solvents were all removed under the examined temperature and duration. In a study in which surfactants effect on the properties of multiwalled carbon nanotubes/polypropylene nanocomposites was examined, TGA showed that sodium dodecyl sulfate (SDS) powder started to decompose at around 200°C and more than 70% weight loss occurred at 300°C [11]. In another study aimed at removing the remnant surfactants and keeping intactness of the CVD SWNT films, sodium dodecylbenzenesulfonate (SDBS) powder started to decompose at 236°C and a heat treatment at 300°C for 5 hr in air was selected [6]. The temperature (i.e., 300°C) selected was between the oxidation temperature of SWNTs and the starting decomposition temperature of surfactants. Among examined surfactants, removal of SDBS showed the best performance in increasing transparency in CNT films, indicating that heat treatment successfully removed the surfactant. Studies on the removal of surfactants in transparent and conductive films (TCFs) made of CNTs have been more often reported for applications in electronic devices rather than sampling devices, including the previous study mentioned above. General approaches to remove surfactants to obtain more conductive TCFs include rinsing, heating, and acid treatment. AD SWNT film produced by a spray method in which the CNTs were suspended in SDS, sprayed on polyethylene terephthalate (PET) film, and rinsed in water several times was immersed in various acids and it was found that HNO_3 could efficiently remove the remaining surfactant [5]. Photocatalysis using ZnO nanoparticles and Fenton reaction were tested to remove surfactants in CVD SWNT film fabricated by filtration method and the removal of residual surfactants was confirmed through Raman and X-ray photoelectron spectroscopy (XPS) spectra [7]. Few studies have examined TGA with BPs [12–14]. Sweetman et al. performed TGA with HiPco BPs fabricated through *meso*-tetra(4-sulfonatophenyl)porphyrin dihydrogen chloride (TSP) and phthalocyanine tetrasulfonic acid (TPS) suspension in air [12]. The mass of both samples remained relatively constant between 200 and 300°C and showed a sharp decrease between 400 and 600°C which is attributable to the decomposition of the dispersants and SWNTs. This behavior is showing a similar pattern to our study. Muramatsu et al. examined the oxygen stability of CVD double-walled carbon nanotube (DWNT) and SWNT BPs (type not specified) in an argon and oxygen (1%) mixture [13]. DWNT-derived BP oxidized at a much higher temperature (717°C) compared with SWNT-derived BP. The oxidation pattern of the SWNT BP was similar to that of our HiPco BPs.

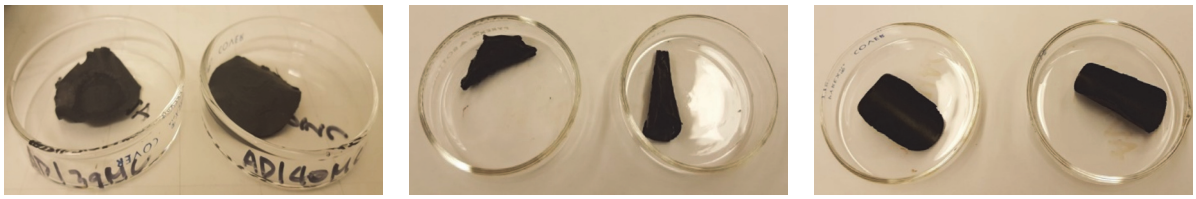
3.2. Heat Treatment. Weight data and images showing the physical appearance of the BPs are shown in Figures 3 and 4, respectively. Acetone-cleaned AD BPs lost approximately 26, 48, and 32% of their weight, whereas methanol-cleaned AD BPs decreased their weight by around 29, 40, and 34% at 300°C for 90 min, 350°C for 60 min, and 300°C for 120 min, respectively. HiPco BPs lost about 22, 5, and 1% at 350°C for 30 min, 300°C for 30 min, and 250°C for 30 min, respectively. However, when we recalculated the weight change from the theoretically predicted weight of AD BPs considering the surfactant effect, +5, −25, and −2% weight of acetone-cleaned AD BP were changed after HT at the first (300°C for 90 min), second (350°C for 60 min), and third (300°C for 120 min) conditions while there were +5, −13, and 0% changes in weight for methanol-cleaned AD BPs. As a result, at the first and third conditions, the weight change of AD BPs was minimal while for HiPco BPs weight change was minimal at the second and the third conditions.

Methanol-cleaned AD BPs either were swirled or become brittle even before heat treatment (Figure 4). Acetone-cleaned AD BPs also showed a similar pattern but only at the first condition, the samples kept the physical integrity. HiPco BPs did not manifest any change in physical integrity throughout the experiment and the samples were very flexible.

3.3. Characterization of Adsorption Properties. As shown in Table 1, acetone-cleaned AD BP had BET surface area with

Table 1: Surface area (SA) and mean pore diameter (d) after heat treatment.

Conditions	Acetone-cleaned AD BP		Methanol-cleaned AD BP		Conditions	HiPco BP	
	SA (m^2/g)	d (nm)	SA (m^2/g)	d (nm)		SA (m^2/g)	d (nm)
300°C, 90 min (1st)	970 ± 18	5.9 ± 0.0	1074 ± 10	5.7 ± 0.0	350°C, 30 min (1st)	887 ± 32	6.6 ± 0.1
350°C, 60 min (2nd)	1228 ± 13	7.1 ± 0.2	1181 ± 31	6.6 ± 0.2	300°C, 30 min (2nd)	933 ± 54	5.6 ± 0.2
300°C, 120 min (3rd)	1226 ± 7	5.8 ± 0.2	1227 ± 33	6.0 ± 0.1	250°C, 30 min (3rd)	697 ± 3	6.2 ± 0.1



(a) (b) (c)

Figure 4: (a) Methanol-cleaned AD BPs before heat treatment and ((b) and (c)) acetone-cleaned AD BPs after heat treatment at 350°C for 60 min (2nd) and 300°C for 120 min (3rd), respectively.

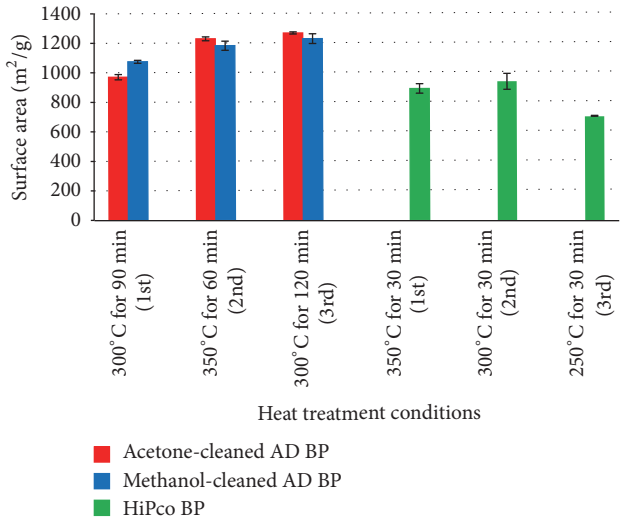


Figure 5: Surface areas comparison.

mean pore width of 970 ± 18 (5.9 ± 0.0), 1228 ± 13 (7.1 ± 0.2), and 1266 ± 7 (5.8 ± 0.2) m^2/g while methanol-cleaned AD BP exhibited 1074 ± 10 (5.7 ± 0.0), 1181 ± 31 (6.6 ± 0.2), and 1227 ± 33 (6.0 ± 0.1) m^2/g at the first, second, and third heat treatment conditions, respectively (i.e., 300°C for 90 min, 350°C for 60 min, and 300°C for 120 min). HiPco BP resulted in 887 ± 32 (6.6 ± 0.1), 933 ± 54 (5.6 ± 0.2), and 697 ± 3 (6.2 ± 0.1) m^2/g at the first, second, and third conditions, respectively (i.e., 350°C for 30 min, 300°C for 30 min, and 250°C for 30 min). Figure 5 compares the BET surface areas between BPs at different heat treatment conditions. Overall, acetone-cleaned and methanol-cleaned AD BPs revealed a similar pattern at all conditions as expected and all conditions yielded a high BET surface area of almost 1000 m^2/g or more which is much higher (at least 2.5 times) than before the heat treatment, 322 and 387 m^2/g for acetone-cleaned and methanol-cleaned AD BPs, respectively [8]. At the second (350°C for 60 min) and third (300°C for 120 min) conditions, both AD BPs showed a relatively higher surface area than that at the first condition (300°C for 90 min). For HiPco BPs, the first (350°C for 30 min) and second (300°C for 30 min) conditions resulted in a relatively higher surface area while the surface area at the third condition (250°C for 30 min) was not much changed compared to before treatment, 649 m^2/g [8].

Since methanol-cleaned AD BPs did not keep their physical integrity during the experiment, only acetone-cleaned AD BPs were considered to be chosen for our next study in which BPs treated with the selected heat treatment conditions will be examined for desorption efficiency through photothermal desorption (PTD). Although the surface area of the acetone-cleaned AD BPs was relatively lower at the first condition (300°C for 90 min), the condition was selected since the samples were physically intact only at that condition and weight change was minimal. On the other hand, the second condition (300°C for 30 min) was selected for HiPco BPs because of the minimal loss in weight and relatively high surface area.

Many studies on the purification of CNT powder through chemical, physical, or a combination of both processes are focused on the removal of metal catalysts and carbonaceous impurities in CNTs [15] and as far as we know this study is the first investigation of the heat treatment effect on BPs to improve the adsorption properties by mainly removing surfactant residues and any impurities involved in the process. From our previous study, it was suggested that surfactants were not completely removed even after cleaning during the fabrication process. Most purification studies employ a combined process of acid treatment (i.e., liquid-phase oxidation) followed by gas-phase oxidation under heat [15–19]. HiPco SWNTs (528 m^2/g) were purified with acids and heat

treatment was selectively performed [16]. Among four acids examined (HCl, HF, H_2SO_4, and HNO_3), HF treated SWNTs for 4–8 hr yielded 635 m^2/g while HF treatment followed by 600°C heat treatment for 6 hours in inert atmosphere showed the highest increase in surface area (1555 m^2/g). However, further heat treatment at 1000°C for 6 hours diminished it to 806 m^2/g, eliminating porous structure. In another study, after the heat treatment of SWNTs (not specified, 298 m^2/g) at 800°C for 2 hours in CO_2 and H_2 environments, surface area was increased to 249 and 351 m^2/g, respectively. 52 and 30% of weight loss occurred in CO_2 and H_2 environments, respectively, while keeping the original pore size distribution of the SWNTs [17]. On the other hand, nitric acid treatment at 70°C for 5 hours changed it completely, resulting in surface area of 544 m^2/g.

Heat treatment in air could have oxidized our samples which possibly changed the chemical property or functionalized the materials but we believe that oxidation was minimal in our study since it was performed in a small sized furnace with only a small vent in which air circulates naturally and in a temperature below which the oxidation of SWNTs powder starts (380–400°C) [6, 9, 10]. A detailed chemical analysis was not performed in this study to determine if all impurities are completely eliminated through the heat treatment; rather, we used a gravimetric method, which did not give us accurate information on the effect of heat treatment in terms of chemical composition. Since the scope of this study was to find a simple way to remove impurities involved in the fabrication process of BP in order to improve adsorption property, surface area analysis was the focus rather than elemental analysis.

4. Conclusions

The effect of heat treatment on the adsorption property was examined on the fabricated AD BP and HiPco BP. Considering the BET surface area data and changes in weight and physical integrity before and after heat treatment, conditions at 300°C for 90 min and 300°C for 30 min were determined to be the most appropriate for acetone-cleaned AD BP and HiPco BP, respectively. With those selected conditions, further investigations on photothermal desorption (PTD) will be followed.

Disclosure

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of National Institute for Occupational Safety and Health (NIOSH) or represent an endorsement by NIOSH.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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