Effect of Oxygen for Enhancing the Gas Storage Performance of Activated Green Carbon

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Abstract: We investigated the gas storage capacity of thermally carbonized and chemically activated Phyllostachys bambusoides (PB), which is a nature-derived green carbon with an organic porous structure. Samples were thermally treated at 900 °C for 24 h, and then were chemically activated with different amounts of KOH. The pore distribution, surface area, and H2 storage capacity were measured by N2 and H2 gas sorption, up to 847 mmHg (1.13 bar) at 77 K. The CO2 storage capacity was measured up to 847 mmHg (1.13 bar) at 298 K. The maximum gas storage was shown in the sample activated with 6 times gravimetric ratio of chemical agent. It reached 1.86 wt% for H2 and 3.44 mmol/g for CO2. We used multilateral analysis methods (XRD, XPS, Raman spectroscopy, and scanning electron microscope) to identify the factors influencing gas sorption. We found that the amount of oxygen groups influence the enhancement of gas storage capacity. Moreover, the results showed that PB-based porous activated carbon has the potential to be used as a multirole gas storage material.

Keywords: Phyllostachys bambusoides; chemical activation; porous activated carbon; gas storage; amount of oxygen group

1. Introduction

As concerns about global warming and the depletion of conventional energy resources continue to increase, growing attention has been focused on the development of gas storage materials for hydrogen and carbon dioxide [1–6]. Carbon-based materials have been investigated for possible use in both fields. In the case of hydrogen storage, since porous carbon materials are light in weight and have fast kinetics due to physisorption [7–11], they have an advantage compared with current hydrogen storage technologies such as low-temperature liquid storage, metallic alloys, and chemical hydrides [5,12–14]. The same advantages make porous carbon materials suitable for capturing other types of gas, such as carbon dioxide (CO2) [4,5,14–21].

It is well known that the specific surface area and pore size are the important factors for enhancing the gas storage capacity [14,22–28]. To increase surface area and make proper sized pores, a chemical activation process using potassium hydride (KOH) as a chemical agent has been employed [28–31]. In the activation process, the carbon frame is etched due to the intercalation of the potassium compounds...
and oxidation. Then, CO\(_2\) production from K\(_2\)CO\(_3\), which is the subsequent reactant, above 700 °C contributes to the further development of pore distribution via carbon gasification \([7,32]\). This process results in a large surface area which enhances storage capability. In addition, the optimum interlayer distance has also been reported to increase storage capacity \([26,27,33,34]\).

Here, we report that the oxygen groups in carbon-based materials play a role for enhancing the adsorption of both H\(_2\) and CO\(_2\). It was achieved with chemical activated green carbon prepared from carbonized *Phyllostachys bambusoides* (PB). The surface area, structure, and morphology were investigated with Brunauer-Emmett-Teller (BET) analysis, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and scanning electron microscopy (SEM). We found that the gas-sorption ability cannot be explained by surface area, interlayer distance, and morphology. The oxygen groups on the graphitic layer are closely related to the gas storage capacity. This result may help bring the field one step further to understanding the gas sorption mechanism in carbon-based materials.

2. Materials and Methods

2.1. Materials and Carbonization

Pristine PB was cut into 50-mm long and 5-mm width sticks. The PB sticks were cleansed two times by sonication in acetone, ethanol, and de-ionized (DI) water for 30 min to remove unexpected residue, such as dust. After cleaning, the samples were dried at room temperature under atmospheric conditions. Then, the PB sticks were carbonized in a tube furnace by thermal treatment. The PB sticks were thermally treated at 900 °C in a N\(_2\) atmospheric condition. The treatment temperature was increased by 5 °C min\(^{-1}\) from room temperature to 900 °C and maintained for 24 h. The PB900 was ground to investigate their structure and gas sorption properties.

2.2. Chemical Activation and Neutralization

Chemical activation was only performed on the carbonized PB treated at 900 °C (PB900), which showed the highest hydrogen storage performance compared to PB treated at other temperatures; 2 g of ground PB900 was mixed with different amounts of chemical agent (KOH) flake (8, 12, and 16 g). The resulting samples were named R4 (Ratio 4, 8 g of KOH), R6 (Ratio 6, 12 g of KOH), and R8 (Ratio 8, 16 g of KOH), respectively. Using DI-water, the mixtures were blended uniformly. The solutions were dried in N\(_2\), at 70 °C, and then the samples were ground. The ground mixture was thermally treated in a tube furnace at 750 °C, under N\(_2\) atmosphere. The treatment temperature was increased by 5 °C min\(^{-1}\) from room temperature to the target temperature and maintained for 1.5 h. The chemically activated sample was dissolved using DI-water to neutralize it. Dissolved samples were centrifuged to isolate the aqueous chemical agents. This aqueous solution was replaced with new DI-water and the sample was centrifuged at 8000 rpm for 3 h. This process was repeated until the solution was completely neutralized.

2.3. Characterization

The neutralized sample was dried and ground. The structure and chemical species of the samples were investigated by X-ray diffraction (XRD, Rigaku, SmartLab, Japan), Raman spectroscopy (Witec, Alpha-300, Germany), and X-ray photoelectron spectroscopy (XPS, ULVAC, PHI-5000 VersaProbe III, Japan). The surface area, pore distribution, and hydrogen and CO\(_2\) storage capacity were characterized by gas analyzer (ASAP 2020, Micromeritics, USA.). The morphology of the samples was observed using a scanning electron microscope (SEM, JEOL, JSM-7800F, Japan).
3. Results and Discussion

3.1. Structural Investigation With XRD, and Raman Spectroscopy

PB is a perennial plant in the bamboo subfamily of Poaceae composed of biological fibers containing cellulose chains. Cellulose, hemicellulose, and lignin are the main components of the cellulose chain in PB. Due to its structural and chemical characteristics, PB has a porous structure and high tensile strength [35]. Pyrolysis of the cellulose chain using thermal treatment causes a change in the PB structure. During thermal treatment, the cellulose changes into thin porous carbon sheets by disintegration and rearrangement, while lignin and hemicellulose are pyrolyzed [36]. The structural changes in the PB depend on the thermal treatment temperature. Among the samples treated at 800, 900, 1000, and 1100 °C, PB900 showed the maximum specific surface area and hydrogen storage capacity [37]. This result was well consistent with the previous reports [38,39]. Accordingly, we chose PB900 as the pristine material for chemical activation.

The structure of the activated PB was investigated by XRD and Raman spectroscopy. Figure 1 shows the XRD patterns and fitted profiles of the PB900, R4, R6, and R8 samples. The inset in Figure 1a shows the XRD pattern of pristine PB; (002) and (100) peaks are shown in all samples, but their intensities differ. As the amount of KOH increased, the intensity of both peaks decreased. Here, we focused on the (002) peak. The height of the (002) peak from the background is defined as $R$, which is the parameter used to identify the aligned carbon layers [40] (See Figure 2). Values of $R$ from PB900, R4, R6, and R8 were 1.75, 1.18, 1.11, and ~1.00, respectively.

![Figure 1](image-url)

Figure 1. (a) XRD patterns of PB, PB900, R4, R6, and R8. XRD (002) sup-peak profile fittings of samples (b) PB900, (c) R4, (d) R6, and (e) R8. The other peaks (arrows) come from the Si and SiO$_2$ substrate.

The number of sub-peaks in the (002) peak increased with the increasing amount of chemical agent. As shown in Figure 1b–e, the numbers of sub-peaks increased from 1 for PB900 to 5 for R8. In the sample PB900 (Figure 1b), there is a single (002) peak at 22.86° corresponding to a $d$-spacing of 3.89 Å. The information on the other samples is presented in Table 1. The existence of various interlayer distances is due to the amorphization of PB900 by the chemical activation. In other words, the structural modulation is induced by etching and collapse processes.
Table 1. XRD (002) sub-peak information of samples.

| Sample | Peak Position ($2\theta$, °) | FWHM ($2\theta$, °) | d-Spacing (Å) |
|--------|------------------------------|--------------------|--------------|
| PB900  | 22.86                        | 9.25               | 3.89         |
| R4     | 21.57                        | 6.47               | 4.12         |
|        | 26.51                        | 8.72               | 3.36         |
| R6     | 17.38                        | 3.50               | 5.10         |
|        | 22.34                        | 5.28               | 3.98         |
|        | 26.27                        | 6.07               | 3.39         |
|        | 31.25                        | 4.67               | 2.86         |
| R8     | 16.01                        | 5.01               | 5.53         |
|        | 20.03                        | 5.24               | 4.43         |
|        | 23.84                        | 4.91               | 3.73         |
|        | 27.01                        | 5.95               | 3.29         |
|        | 31.52                        | 4.96               | 2.84         |

This behavior was also observed in the Raman study. The inset in Figure 3a shows the normalized Raman spectrum of pristine PB. The two peaks at 1600 and 2948.2 cm$^{-1}$ correspond to the typical feature of lignin [40,41]. As shown in Figure 3a, the Raman spectrum has $D$, $G$, and $2D$ peaks, which are consistent with the previous studies of carbon materials [42–44]. In more detail, the $G$ and $D$ peaks consist of the first-order bands of $G$, $D$ ($D1$), $D2$, $D3$, and $D4$ as shown in Figure 3b–e.

$G$ and $D$ relevant bands originate from the highly ordered ideal graphitic lattice ($E_{2g}$ vibrational mode) and the disorder of the graphitic lattice ($A_{1g}$ vibrational mode), respectively [45–48]. Among the relevant $D$ peaks, the $D2$ band at 1670 cm$^{-1}$ which is observed on the shoulder of the $G$ band, corresponds to the graphitic lattice mode of $E_{2g}$ symmetry like $G$ band, but indicates disorder on the surface carbon layer [46,49]. Due to the collapse of the graphitic sheet structure, the ratio of the integrated areas of the $G$ band and $D2$ band ($I_{D2}/I_G$) decreases as the ratio of KOH increases. The $D3$ band, which appears at 1500 cm$^{-1}$, is specifically related to an amorphous carbon structure [49–51]. The ratio of the integrated areas of the $G$ band and $D3$ band ($I_{D3}/I_G$) increased to 1.16, 1.20, 1.41, and 1.48, as the amount of chemical agent increased. The ratio of total disordered defects in the structure ($I_{D-Total}/I_G$) also increased to 5.26, 5.29, 5.43, and 5.72 with the increase in chemical agent (peak details are in Table 2). These results indicate that the disordered carbon structure becomes larger due to the chemical agent.
Figure 3. (a) Normalized Raman spectra of samples PB, PB900, R4, R6, and R8. Sub-peak fitting of the D and G regions for samples (b) PB900, (c) R4, (d) R6, and (e) R8.

Table 2. Peak details of D and G region sub-peak fitted profiles obtained from Raman spectroscopy.

| Band | Parameters | PB900 | R4 | R6 | R8 |
|------|------------|-------|----|----|----|
|      | Raman shift (cm$^{-1}$) | 1589  | 1591 | 1587 | 1587 |
| G    | FWHM (cm$^{-1}$)       | 71.53 | 75.23 | 72.04 | 66.45 |
|      | Integrated Area        | 51.43 | 49.45 | 51.15 | 44.92 |
|      |                       | 1348  | 1344 | 1340 | 1338 |
| D (D1)| Raman shift (cm$^{-1}$) | 152.2 | 147.9 | 148.1 | 142.0 |
|      | FWHM (cm$^{-1}$)       | 125.2 | 122.5 | 126.9 | 124.3 |
|      | Integrated Area        | 2.43  | 2.48 | 2.48 | 2.77 |
|      |                       | 1662  | 1672 | 1669 | 1663 |
|      | Raman shift (cm$^{-1}$) | 94.21 | 65.79 | 86.07 | 60.59 |
|      | FWHM (cm$^{-1}$)       | 10.82 | 7.94 | 7.91 | 5.36 |
|      | Integrated Area        | 0.21  | 0.16 | 0.15 | 0.12 |
|      |                       | 1513  | 1509 | 1511 | 1511 |
| D2   | Raman shift (cm$^{-1}$) | 129.9 | 141.8 | 150.1 | 151.1 |
|      | FWHM (cm$^{-1}$)       | 59.54 | 59.35 | 72.27 | 66.67 |
|      | Integrated Area        | 1.16  | 1.20 | 1.41 | 1.48 |
|      |                       | 1211  | 1227 | 1209 | 1215 |
| D3   | Raman shift (cm$^{-1}$) | 298.0 | 292.9 | 292.4 | 287.2 |
|      | FWHM (cm$^{-1}$)       | 75.03 | 71.95 | 70.75 | 60.45 |
|      | Integrated Area        | 1.46  | 1.46 | 1.38 | 1.35 |

3.2. X-ray Photoelectron Study before and after Chemical Activation

Figure 4 depicts the XPS survey and fitted spectra of the PB900 and R6 samples (data for all samples are in Figure 5). As shown in Figure 4a,d, PB900 and R6 contain mainly C and O. Figure 4b,e are the XPS Cls peaks of PB900 and R6, respectively. sp$^2$ (C=C), and sp$^3$ (C-C) bonding were observed and each chemical species were barely changed (peak position, full width at half maximum (FWHM), and atomic concentration) after the chemical activation process. Figure 4c,f are the XPS O1s peaks for PB900 and R6, respectively. C-O, and C=O species were observed in PB900 and O–C=O species additionally appear in the R6 (Table 3). These three types of bonds are respectively from the phenol and ether groups, carbonyl groups, and lactone groups [52–55]. The appearance of lactone groups is probably due to the attachment of oxygen atoms in the vacancies of the collapsed graphitic structure.
The atomic concentration ratio of oxygen increases when the sample has been chemically activated (Table 4). It is worth noting that the maximum oxygen ratio was observed in sample R6, but not in sample R8. The results indicate that the chemical activation process using a specific amount of KOH increases the surface oxygen groups.

**Figure 4.** XPS results of PB900 and R6. (a) XPS survey, (b) C1s, and (c) O1s of PB900. (d) XPS survey, (e) C1s, and (f) O1s of R6.

**Figure 5.** XPS results of samples. XPS survey of (a) PB900, (b) R4, (c) R6, and (d) R8. C1s region fitted spectra of (e) PB900, (f) R4, (g) R6, and (h) R8. O1s region fitted spectra of (i) PB900, (j) R4, (k) R6, and (l) R8.
Table 3. Peak details of chemical species fitted profiles obtained from XPS results.

| Element (Chemical Species Indication) | Parameters | PB900 | R4 | R6 | R8 |
|--------------------------------------|------------|-------|----|----|----|
| **C** Sp$^1$ (C−C)                   | Position (eV) | 285.4 | 285.3 | 285.2 | 285.2 |
|                                      | FWHM (eV)   | 1.59  | 1.77  | 1.57  | 1.90  |
|                                      | Integrated Area | 1207.1 | 1308.4 | 915.9 | 759.1 |
|                                      | Concentration (%) | 22.42 (30.06) | 18.90 (29.03) | 16.45 (28.72) | 19.59 (30.33) |
| **C** Sp$^2$ (C=C)                   | Position (eV) | 284.5 | 284.4 | 284.4 | 284.4 |
|                                      | FWHM (eV)   | 1.03  | 1.03  | 1.05  | 1.05  |
|                                      | Integrated Area | 2808.6 | 3319.4 | 2273.5 | 1744.0 |
|                                      | Concentration (%) | 52.16 (69.94) | 46.21 (70.97) | 40.83 (71.28) | 38.72 (69.67) |
| **O** C−O                           | Position (eV) | -     | -     | 532.8 | 532.8 |
|                                      | FWHM (eV)   | -     | -     | 2.56  | 2.12  |
|                                      | Integrated Area | -     | -     | 1004.2 | 188.8 |
|                                      | Concentration (%) | -     | -     | 15.91 (62.59) | 9.64 (28.15) |
| **C**=O                             | Position (eV) | -     | -     | 531.1 | 531.1 |
|                                      | FWHM (eV)   | -     | -     | 2.36  | 2.66  |
|                                      | Integrated Area | -     | -     | 1411.2 | 1577.8 |
|                                      | Concentration (%) | -     | -     | 52.16 (69.94) | 38.72 (69.67) |
| **O−C=O                             | Position (eV) | -     | -     | -     | -     |
|                                      | FWHM (eV)   | -     | -     | -     | -     |
|                                      | Integrated Area | -     | -     | -     | -     |
|                                      | Concentration (%) | -     | -     | 15.91 (62.59) | 9.64 (28.15) |

The values in bracket of concentration indicate the “In-region concentration” of species.

Table 4. Atomic concentrations in PB900, R4, R6, and R8 obtained from XPS results (%).

| Element (Primary Region) | PB900 | R4 | R6 | R8 |
|--------------------------|-------|----|----|----|
| C (C1s)                  | 74.58 | 65.11 | 57.28 | 64.61 |
| O (O1s)                  | 25.42 | 34.89 | 42.72 | 35.39 |

3.3. Surface Structure and Gas Adsorption Using BET Analysis

Porous carbon structure develops due to the chemical activation process (see Table 5). The specific surface areas ($S_{BET}$) of R4, R6, and R8 are 590, 842, and 1150 m$^2$/g, respectively. It is well known that the gas sorption capacity increases as the surface area increases. In the result of the pore size distribution (PSD) obtained from the density functional theory (DFT) method, every sample shows the highest distribution between 5–7 Å of pore width (1.89 cm$^3$/g at 0.68 Å for R8, 1.36 cm$^3$/g at 0.68 Å for R4, 1.16 cm$^3$/g at 0.68 Å for R6, and 0.65 cm$^3$/g at 0.64 Å for PB900). We found that the maximum capacity reaches 1.86 wt% (77 K, 847 mmHg) for H$_2$, and 3.44 mmol/g (298 K, 847 mmHg) for CO$_2$. These results surpassed the capacity of the previously commercialized porous activated carbon (PAC, 1.23 wt% at 1 bar/77 K for H$_2$, and 2.1 wt% at 313 K for CO$_2$) [17,29], but their capacity is lower than the results observed for chemically activated bamboo species in previous studies (2.74 wt% at 1 bar/77 K for H$_2$, and 4.5 mmol/g at 1 bar/298 K for CO$_2$) [56,57]. However, we focused on finding other factors for enhancing the storage capacity. Interestingly, the maximum storage capacity was exhibited in R6, but not R8, even though the surface area of R8 is larger than that of R6 (See Figure 6). This shows that the surface area does not completely reflect the gas sorption capability. Hence, we investigated the other factors related to the strange capacity.

Table 5. Pore structure of samples confirmed by BET analysis. ($S_{BET}$: Specific surface area by BET plot, $V_{t-mic}$: Micropore volume by t-plot (<2 nm), $V_{meso}$: Mesopore volume, $V_{tot}$: Total pore volume, $D_{avg}$*: Average pore diameter by BET plot (4 V/4A), $W_{HK}$: Average pore diameter by H-K method (<2 nm)).

| Sample | $S_{BET}$ (m$^2$/g) | $V_{t-mic}$ (cm$^3$/g) | $V_{meso}$ (cm$^3$/g) | $V_{tot}$ (cm$^3$/g) | $D_{avg}$* (nm) | $W_{HK}$ (nm) | H$_2$ Uptake (wt%) at 77 K | CO$_2$ Uptake (mmol/g) at 298 K |
|--------|---------------------|------------------------|-----------------------|---------------------|-----------------|-----------|-------------------------|-------------------------------|
| PB900  | 680                 | 0.26                   | 0.03                  | 0.29                | 1.71            | 0.55      | 1.35                    | 2.20                          |
| R4     | 590                 | 0.21                   | 0.01                  | 0.22                | 1.60            | 0.54      | 1.48                    | 2.98                          |
| R6     | 842                 | 0.43                   | 0.05                  | 0.48                | 2.26            | 0.56      | 1.86                    | 3.44                          |
| R8     | 1150                | 0.43                   | 0.03                  | 0.46                | 1.30            | 0.58      | 1.82                    | 3.34                          |
First, we focused on the (002) peak in the XRD results. The R6 and R8 samples developed 5.10 and 5.53 Å of interlayer distance. Previously, it was reported that 5.0–7.0 Å of interlayer distance was the optimum interlayer distance for H\textsubscript{2} adsorption in carbon materials [26,27,58–62]. Second, we assumed that the morphology also affected the storage capacity. Therefore, the morphology of the sample was studied with SEM. Figure 7 shows the SEM image of the PB900, R4, R6, and R8 samples. The overall particle size decreased with increasing chemical agent (Figure 7a–d). For sample R8, no particles over 100 um were observed. The magnified images are presented in Figure 7e–h. Note that exfoliation of thin carbon sheets was observed in sample R6 (Figure 7g), before the sample was broken to the small pieces shown in R8 (Figure 7h). However, these two factors, interlayer distance and morphology of the samples, do not provide the appropriate information of enhancing storage capacity in R6.

Finally, we considered the amount of oxygen groups, because the theoretical investigation for the interaction between hydrogen and oxygen on the graphite basal plane was reported [63]. In the XPS results, we found that O–C=O bond appeared only in R6 and R8. Note that the maximum amount of oxygen groups is shown in R6 and the amount of O–C=O species (integrated area) in R6 is larger than that of R8 (Table 3). Water solubility is determined by the different amount of oxygen groups.
Hence, we dispersed the samples in DI water (see Figure 8). To determine solubility, 5 mg of each sample was diluted with 400 mL of DL water and sonicated for 3 h, and then put on the table for 12 h. The highest solubility was shown in R6. As mentioned above, this result is attributed to the largest amount of oxygen groups in R6 and show that the oxygen functional groups, especially O-C=O bond on the graphitic basal plane, are one of the factors for enhancing the gas storage capacity.

Figure 8. The optical image of PB900 and activated PB after dispersion. The highest solubility is shown in R6.

4. Conclusions

In summary, PB-based PAC was prepared using thermal treatment and KOH-based chemical activation. The chemically activated PB-based PAC samples were basically composed of carbons. However, their amorphous structure increased after chemical activation, and this tendency increased when the amount of chemical agent was increased in the chemical activation process. The chemical composition and the structural characteristics were confirmed by XPS, Raman spectroscopy, XRD, and BET analysis. The maximum H$_2$ and CO$_2$ uptake 1.86 wt% (1.13 bar, 77 K) for H$_2$ and 3.44 mmol/g (1.13 bar, 298 K) for CO$_2$ were exhibited by sample R6. We established that the amount of oxygen groups, especially the lactone groups, play a very important role in enhancing both H$_2$ and CO$_2$ uptake of nanoporous carbon. The surface area, interlayer distance, and the morphology of the samples effect gas storage capacity, but this should be studied in details in our further investigations. We therefore suggest that the oxygen groups on the graphitic layer can also have an effect on increasing the gas sorption capacity.

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