Carbon materials derived from rice husks at low and high temperatures

G J H Melvin1, *, Z Wang2, N J Siambun1, M M Rahman1

1 Faculty of Engineering, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, Malaysia.
2 Institute of Carbon Science and Technology, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan.

*E-mail: melvin.gan@ums.edu.my

Abstract. Rice husk (RH) can be classified as an agriculture residue, majorly produced from by-product of rice milling industries. However, RHs are only mainly utilized for low value energy resource. A great number of researches and innovations have shown that heat treated RHs can turn into valuable carbon materials. In this study, the RHs were carbonized at 800°C and 2500°C, respectively. Their structure, morphology, elemental composition, and quality were characterized using transmission electron microscopy, X-ray photoelectron spectroscopy, and Raman spectroscopy. The carbon materials obtained from low and high temperature carbonization processes showed different characteristics. High purity and crystallinity of carbon materials were obtained from RHs carbonized at 2500°C. Furthermore, from Raman results, RHs carbonized at 2500°C exhibited low D/G ratio. This further reveals that the RHs carbonized at 2500°C possess minimal defects. The unique characteristics of RHs carbonized at high temperature indicate that they could be a promising material to be utilized in particular or various applications.

1. Introduction
Carbon materials including fullerene, carbon black, carbon fiber, carbon nanotubes, graphene, porous carbon, and their other derived forms; due to their distinctive physical and chemical characteristics, have received considerable attention, from fundamental research to wide range of applications [1, 2]. However, these carbon materials can be considered as high-grade carbon materials, which are high in cost and rarely available in bulk quantity. In order to obtain carbon materials with low cost fabrication process and more environment friendly technique, carbonization of waste materials can be considered as a beneficial method. Since the waste materials are available in large scale, greener technology to produce bulk quantity of valuable carbon materials from waste materials can be promoted. Waste materials can be in the form of agricultural or organic wastes, synthetic compound wastes, and so on. Several conventional sources for carbon materials are methane, ethane, acetylene, benzene, and another hydrocarbon based fossil fuel [2]. In comparison with the waste materials as the source to obtain carbon materials, their lacks in abundance and comparatively high cost have been the drawback for their usage, for particular cases. For instance, green nanocomposites [3], supercapacitors [4, 5], conductive materials [6], adsorbent materials [7], and so on, are some examples of usage of carbon materials derived from waste materials.
Rice husk (RH) can be categorized as an agriculture residue, mainly produced from by-product of rice milling industries [8, 9]. From a statistic, it was reported that the annual rice production is approximately 500 million tons in developing country, and the RH available to be utilized is approximately 100 million tons [8]. Commonly, RHs are exploited as low value energy resource or simply burnt at the field as they are considered as a waste, which will greatly affect the air quality and unfavorable to the environment [9]. Thus, it is important to conduct research on RHs and then utilize them comprehensively. RH contains organic materials such as lignin, hemicellulose, and cellulose, which is in favor to turn them into raw carbon materials [10]. A great number of researches and innovations have shown that heat treated RHs can turn into valuable carbon materials [8-10]. Based on the consideration regarding cost, environment issues, production quantity, and so on, RHs can be considered as a strong candidate to be fully utilized as the source of carbon materials.

Generally, in order to obtain high-grade carbon materials, most of the synthesis, chemical process or reactions are necessary. Alternatively, carbonization process, through heat treatment can be considered as an advantageous method. Diverse structure and morphology of carbon materials derived from waste sources can be obtained, depending on the parameters such as heat temperature control in the carbonization process [11, 12]. In this study, the RHs were carbonized at low temperature of 800°C and high temperature of 2500°C. Then, their structure, morphology, elemental composition and quality were characterized and compared.

2. Experimental

Dried RHs without further modification were used as the source to be carbonized. Two RH samples were prepared and carbonized at different temperatures of 800°C and 2500°C. First, the raw RHs were carbonized at 800°C, 1 h using furnace, under the presence of argon gas. Next, the carbonized RHs at 800°C were again loaded into graphite box, further heat treated at 2500°C, 0.5 h using graphite resistance furnace operating in a high purity argon gas atmosphere at 760 Torr. Both samples were cooled down naturally and then grounded into powder form before conducting further evaluation. RHs carbonized at 800°C will be denoted as LTRH (low temperature) and RHs carbonized at 2500°C will be denoted as HTRH (high temperature), hereafter.

The samples were observed using transmission electron microscopy (TEM; JEM-2100F, JEOL) operated at 200 kV, in order to investigate the structure and morphology. X-ray photoelectron spectroscopy (XPS; PHI Quantera II) was performed to characterize the elemental composition. Raman spectroscopy measurement was performed on a Raman spectrometer (Renishaw inVia Raman spectroscope) with 532 nm laser excitation, in order to determine the quality of carbon materials derived from RHs at low and high temperatures.

3. Results and discussions

TEM images are shown in figure 1. From figure 1(a), LTRH indicate that they can be considered as disordered carbon form or amorphous carbon and no clear edges were observed. Commonly, carbon materials derived from waste materials at low temperature, such as 800°C, will produce porous carbon [4, 5]. Conversely for HTRH, from figure 1(b), mixture of flattened graphene, wrinkled graphene, and partially carbon cage can be observed. Furthermore, they also exist in the nanometer size range, which includes few- and multi-layer graphene layers. Moreover, no amorphous carbon was observed on the graphene surface. Heat treatment at 2500°C produced clean surface, clear edges, and relatively high crystallinity of carbon materials. This can be attributed to the realignment or restructure of vapor carbon at high temperature [12]. The carbons vaporized at high temperature, and their deposition during the cool down process, contributed to the structure formed by HTRH.
XPS evaluation was conducted to determine the elemental composition of the RHs heat treated at low and high temperatures, and the results are as depicted in figure 2(a). Both XPS wide survey spectra confirmed the presence of carbon (C 1s) peak at around 284 eV and oxygen (O 1s) peak at around 533 eV. Clearly, in contrast with HTRH, LTRH showed Si 2s and Si 2p (silicon) peaks. This might be attributed to the silica absorption of rice plants in the form of silicic acid from the soil [13]. Commonly, heat treated RHs at low temperatures (around 600~1000°C) will have main components of carbon and silica, depending on certain conditions [14, 15]. For HTRH, clear C 1s peak can be observed, with almost no other elements, and this implies that they are in the form of high purity carbon materials. However, extremely low oxygen (O 1s) peak was observed too, might be attributed to oxygen absorption when exposed to the environment. Interestingly, combination of TEM and XPS evaluation, RHs carbonized at 2500°C show graphene layer structure with high crystallinity and high purity of carbon.
Raman spectroscopy is a nondestructive and an effective tool to probe structure at the atomic scale on the basis of vibrational symmetry. Generally, characteristic bands such as D band (disorder-induced band that is often associated with defective graphite structures) at around ~1350 cm\(^{-1}\) and G band (graphite band) at around ~1580 cm\(^{-1}\) can be observed for various carbon materials. Raman spectra for LTRH and HTRH are illustrated in figure 2(b). For HTRH, clear D and G peak can be observed. For LTRH, the trend of moving upward spectra can be attributed from the broadening of D peak or affected by SiC peak usually traced at lower wavenumber. Nevertheless, the spectra shows certain similarity with low sp\(^3\) amorphous carbon [16]. The D and G peak position, full width at half maximum (FWHM) for D and G peak, and relative intensity of D and G peak (\(I_D/I_G\)) are tabulated in table 1. The position of D peak for LTRH and HTRH has high similarity. The position of G peak for LTRH shifted to higher wavenumber, caused by the broad D peak, as mentioned earlier. Even though direct comparison cannot be concluded for FWHM between LTRH and HTRH, for both D and G peaks, the FWHM values of HTRH showed that they are high crystalline quality with some defects introduced, as depicted in figure 2(b). The \(I_D/I_G\) is associated with the amount of structural defects of carbon materials, and thus provides direct information about the quality of carbonized RHs. The \(I_D/I_G\) for HTRH is calculated to be 0.23, which is comparatively lower than other carbon materials or RHs carbonized at lower temperature [17, 18]. However, based on the existence of D peak, defects are still detectable in both of our samples, regardless they are heat treated at low or high temperatures. One of the reasons, the defects might be introduced to the samples when they are grounded before Raman evaluation. It is worth to notice that D peak also can be found in most of graphitic carbons, which might be due to the defects on the edges, or in our case the carbon cage induced. For comparison, Raman information for multi-walled carbon nanotubes (MWCNT, \(d = 40–70\) nm) was also included in table 1. The position of D and G peak is in the typical range for MWCNT. The D and G peak of MWCNT have high similarity, thus contributed to similar FWHM. Noticeably, the \(I_D/I_G\) is also higher than HTRH, although no modification was conducted to the MWCNT. Commonly, modification will be conducted to improve the dispersion of MWCNT, which also will further introduce defects (higher \(I_D/I_G\)). For carbonized RHs, regardless their carbonization temperature, the D peak appears at lower wavenumber than MWCNT. Furthermore, FWHM of HTRH is also lower than MWCNT, which can be associated with sharper G peak of HTRH. This further indicates that the HTRH are in the high carbon crystalline quality form.

| Sample | D peak (cm\(^{-1}\)) | FWHM for D (cm\(^{-1}\)) | G peak (cm\(^{-1}\)) | FWHM for G (cm\(^{-1}\)) | \(I_D/I_G\) |
|--------|---------------------|-------------------------|---------------------|-------------------------|-------------|
| LTRH   | 1339.7              | -                       | 1595.8              | -                       | -           |
| HTRH   | 1339.8              | 51.2                    | 1569.9              | 23.4                    | 0.23        |
| MWCNT  | 1344.1              | 52.6                    | 1577.1              | 52.9                    | 0.96        |

4. Conclusions
Two types of carbon materials derived from RHs were prepared, namely RHs heat treated at 800°C (LTRH) and RHs heat treated at 2500°C (HTRH). Their structure, morphology, elemental composition and quality evaluations were carried out through TEM observation, XPS evaluation, and Raman measurement. Few and multilayer graphene can be obtained from high temperature treated RHs. Furthermore, high purity and crystallinity carbon material also can be obtained from high temperature treated RHs. From Raman results, RHs carbonized at 2500°C also can be considered as high carbon crystalline with minimal defects. The features of RHs carbonized at high temperature imply that they could be a prominent material to be manipulated in wide variety of applications.
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