Carbon nanostructured materials, including nanosheets, are being produced from a variety of natural waste materials. The process involves activation and carbonization. Potassium hydroxide (KOH) is a well-known chemical agent used to generate pore structure and to prepare the micro/nanostructure of carbon. This study compares the effect of the state of KOH (solid or solute) on carbon formation in peanut shells. Carbon nanosheets were formed from peanut shell by activation with KOH and heat treatment. The surface microstructure and individual carbon nanosheets of peanut shell were found to be more distinct after treatment with solute KOH compared to treatment with solid KOH. This suggests that solute KOH treatment is a simple, cheap, and effective method for producing carbon nanosheets from peanut shells.

Keywords: Natural waste materials, carbonaceous materials, carbon nanosheets

Introduction

The formation of nanostructured materials from waste materials has appeared in recent years [1]. Nanocarbon materials derived from natural waste materials reveal diversity, and high-performance nanostructured carbon materials can be synthesized from waste materials. There are different methods for synthesizing carbon materials. However, many of these techniques are highly complicated, toxic, and expensive. Therefore, the search is on for cheap, abundant natural waste materials to help protect the environment in the production of carbon materials [2–6]. More recent advancements using waste or recycled materials offer great opportunities, as synthesized reinforcements can be produced in situ economically. Carbon materials such as graphene, carbon fibers, and carbon nanotubes are outstanding in mechanical and physical properties [7]. Nanocarbon materials have become important due to their good physical and mechanical properties and high performance in composite materials [8–19].

The preparation of carbon material involves two main steps. First, the raw materials are pre-carbonized in an inert atmosphere to produce carbonaceous materials, and then the carbonized carbon is carried out by carbonization and chemical activation process with chemical agents. Potassium hydroxide (KOH) activation is a well-known method to generate the pore network in carbons. The process of activation by KOH involves two main mechanisms contributing to chemical activation. The first consists of the consumption of carbon by oxygen, producing carbon monoxide and carbon dioxide; this process is catalyzed by alkali metals. The second consists of the reduction of the hydroxide to free potassium metal, the penetration of free metal into the lattice of the carbon, the expansion of the lattice by the intercalated potassium, and the rapid removal of the intercalate from the carbon matrix [2, 12–15, 18, 20–26].

Many researchers [12–14, 22–25] have demonstrated that nanostructured carbon materials can be synthesized from low-cost waste materials with a KOH activation and carbonization process. KOH aqueous (solution) activation was used to prepare porous carbon nanosheets from comcrob waste material to apply as cathodes for lithium-sulfur [12]. Honeycomb-like porous carbon was prepared from pine cone flowers by carbonization at 900 °C and alkali treatment with an aqueous solution of KOH [22]. Micro-mesoporous carbon, prepared from soybeans using a KOH aqueous solution, stirred, and heat treated under nitrogen atmosphere, is reported to be an excellent electrode material in various applications [23]. KOH (solid) was used to activate carbon while porous carbon sheets (used in super capacitors) were derived from water hyacinth [13] and waste coffee grounds [14] by in situ carbonization and activation. Interconnected open-channel carbon nanosheets were prepared from agro-waste pine-apple leaf fiber using a simple hydrothermal technique and KOH chemical activation followed by heat treatment under inert atmosphere [24]. Peanut shell-derived few-layer graphene (PS-FLG) was prepared using KOH activation followed by mechanical exfoliation in 10% H₂SO₄ aqueous solution through probe sonication [25].

Researchers have used KOH in either its solid or solute state for activating and producing carbon nanostructures from a variety of natural waste materials. However, nobody has compared the effect of the state of KOH (solid or solute) on the carbon formation of peanut shells. Peanut (Arachis hypogaea) is a major crop widely distributed throughout tropical and subtropical parts of Asia, Africa, Oceania, North and South America, and Europe [27]. World peanut production reaches approximately 29 million metric tons per year, where the leading producer is China, followed by India and the USA [28]. World annual production of shelled peanuts was 42 million tons in 2014 [29]. Natural structures of peanut shell consisting of cellulose, hemicellulose, and lignocellulose are the major contents of biomass, which can play the role of carbon precursors in producing highly ordered nanocarbons [6, 13]. Waste peanut shells, generated in large volume annually, are considered lignocellulosic biomass waste [30]. This article focuses on the effect of chemical activation with potassium hydroxide (solid and solute) on the formation of peanut shell carbon nanosheets (PSCNS). This low-cost process using the chemical activation and carbonization is used to produce carbon nanostructured material from agro waste in simple steps, adding value to the products.

Experimental Procedure

Sample Preparation and Pre-carbonization Methods. The peanut shell (5 g) was washed and dried at 80 °C for 24 h, treated by HCl 0.5 M for 24 h for removing metallic oxide or organic compounds [13], and then washed by distilled water and dried at 80 °C for 24 h. The pre-carbonization process was carried out at 450 °C for 2 h in a stainless steel tube furnace under argon atmosphere.
Activation with KOH (Solid) and Carbonization Methods of the PSCNS. The pre-carbonized peanut shell (0.5 g) was mixed with KOH (solid) at a mass ratio of 1:1 and milled for 1 h by mortar. Then, the mixed peanut shell was heat treated at 800 °C for 1 h in a stainless steel tube furnace under argon atmosphere. After this process, carbon was extracted from KOH containing mixture with ethyl acetate [31].

Activation with KOH (Solute) and Carbonization Methods of the PSCNS. The pre-carbonized peanut shell (0.5 g) was milled for 1 h by mortar, then stirred into aqueous KOH (solute) with a weight ratio of pre-carbonized peanut shell–KOH = 1:1 for 2 h, and dried at 80 °C for 24 h. Next, the mixed peanut shell was heat treated at 800 °C for 1 h in a stainless steel tube furnace under argon atmosphere. After this process, carbon was extracted from KOH containing mixture with ethyl acetate [31].

Finally, to separate the layer structure of carbon, the activated peanut shell was treated with 10% H2SO4 solution (exfoliation), stirred for 1 h, and then washed with distilled water and dried at 80 °C for 24 h [25].

The schematic illustration of the preparation of carbon nanosheets from peanut shell is shown in Figure 1. The microstructure and morphology of the samples were investigated by scanning electron microscopy (SEM, HITACHI S-4800, ZEISS EVO-MA10), the chemical composition was analyzed by energy-dispersive X-ray spectrometry (EDS, BRUKER AXS), and the crystal structure and the phase purity were examined using X-ray diffraction (XRD, BRUKER D8 ADVANCE CoKα X-ray source).

Results and Discussion

Peanut shell, an agro-waste material, was used to prepare carbon nanosheets by chemical and thermal processes. The microstructure of the raw peanut shell (Figure 2) reveals agglomerates with interconnected hollows and micro-sized pores on the surface. The main elements are carbon and oxygen with a small amount of other elements as shown in Figure 2(c) and Table 1.

The PSCNS activated with solid KOH shows multilayer thin plates in Figure 3(a)–(c). It can be seen that the treated
| Samples                          | C    | O    | Zn   | Cl   | Si   | K    | Ca   | S    |
|---------------------------------|------|------|------|------|------|------|------|------|
| Raw peanut shell                | 61.55| 37.69| 0.72 | –    | 0.04 | –    | –    | –    |
| PSCNS activated with KOH (solid)| 90.51| 7.12 | –    | 1.13 | 0.63 | –    | –    | 0.62 |
| PSCNS activated with KOH (solute)| 84.86| 12.39| –    | 0.81 | 0.95 | 0.25 | 0.38 | 0.37 |

Figure 3. SEM micrographs of peanut shell mixed with KOH (solid) and heat treated at 800 °C for 1 h after exfoliation processing (a) at 10.00 kX, (b) at 15.00 kX (1), (c) at 15.00 kX (2), and (d) average EDS spectrum composition (see Table 1)

Figure 4. SEM micrographs of peanut shell mixed with KOH (solute) and heat treated at 800 °C for 1 h after exfoliation processing (a) at 10.00 kX, (b) at 15.00 kX (1), (c) at 15.00 kX (2), and (d) average EDS spectrum composition (see Table 1)
Figure 5. XRD pattern of peanut shell carbon at 800 °C for 1 h. The microstructure of nanosheets in the KOH (solute) condition shows flat surfaces and better dispersion of carbon nanosheets than for KOH (solid) activation. The smallest thickness of peanut shell carbon nanosheets from this process is less than 50 nm. The chemical (KOH and H$_2$SO$_4$) and thermal activation affects the formation of carbon and the separation of carbon layers to form layers of graphene.

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**Conclusions**

Carbon nanosheets were successfully synthesized from peanut shell by treating with KOH (solid and solute) and carbonization...