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Augmentation of graphite purity from mineral resources and enhancing % graphitization using microwave irradiation: XRD and Raman studies

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ABSTRACT

Processing of graphite from its ore has been studied for more than a decade due to the elevated demand for graphite which has a wide range of applications but restricted to the short availability of resources. In the present study, microwave irradiation was used for the graphitization of carbon using different metal (Ni, Co, Fe, Cr) salts as catalysts. Microwave irradiation excels from the classical thermal treatment since in the former case the reaction time and the temperature used is low. The graphitization using nickel sulfate as a catalyst was most effective when compared to the other catalysts and the % degree of graphitization was about 98% for 5 min of reaction time. The mechanism underlying the formation of graphite by microwave irradiation is also discussed in brief. Hence this study provides a new approach for processing graphite by a simple, fast and effective microwave technique. In addition, the preparation of graphene oxide (GO) from the graphitized carbon was also attempted and compared with GO prepared from commercial graphite.

1. Introduction

Carbon-based materials have been the focus of research over the past years owing to their astonishing electronic and thermal conductivities, good mechanical stability, efficient adsorption capability and chemical stability. With the advantage of these properties, it can be used in various applications. One important candidate from carbon family is graphene, which has been in the spotlight of research. Graphene due to its extraordinary properties can be used in the fields, such as fuel cells, solar cells, lithium ion batteries, supercapacitors, catalyst, photocatalysis and also in targeted drug delivery since graphene is also biocompatible [1,2]. So, preparation of graphene and graphene-based materials is a significant field of research, where graphene is synthesized from graphite precursor by various techniques i.e. based on top down and bottom up approaches [3]. Even though researcher's attention is focussed on graphene, nano-carbons and graphene oxide (GO), the demand for graphite still relishes being on the summit.

Graphite has a wide range of applications such as carbon steel forging, crucibles, refractory bricks, lubricants, dry cell batteries, fuel cells, solar cells, sensors, nuclear production and also in the preparation of most sought out material graphene [4]. China is considered the world's largest producer of graphite as of 2016 and accounts for 780,000 MT of production. As per US Geological Survey, the production of graphite was about 66%, out of which 35% of intake was by China itself. The world production of graphite was over a million metric tons by 2012. Even though graphite has the high production rate, it is also designated as ninth supply risk material [5]. Researchers use different forms of graphite for different applications. There is a wide gap between the quality of graphite obtained from mineral resources and the one used for commercial preparation. To reduce this gap and do make use of the Indonesian graphite resources from Sumatra - Kalimantan island [6] respectively, the crystalline nature of graphite must be tailored and enhanced in par with the commercial graphite. The rationale behind this is the major availability of natural graphite is amorphous in nature, with low quality and restricted accessibility. Still, many researchers focus on the preliminary processes for mining graphite with improved crystallinity [6,7].

Generally, graphite occurs in nature in one of the three forms such as amorphous (70–80%), crystalline flakes (90–98%) and crystalline lump or vein (90–99%) [5,6]. Hence to formulate the applications that emerge from graphite either directly or indirectly, an efficient process is required to obtain natural graphite with good crystallinity and purity from mineral resources. In particular, the demand for the large-sized crystalline graphite flakes is highly preferred. Processes such as grinding, crushing and other mechanical treatment techniques during

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mineral processing may destroy the crystallinity of the graphite and, thus, further processing is required [6,8]. So efforts are desired to obtain graphite economically with improved crystallinity after the preliminary treatment from the mineral.

Various methods were reported for the graphitization such as template method, pyrolysis, foaming technique, chemical activation followed by catalytic graphitization, plasma enhanced chemical vapour deposition and so on [1]. Mostly these techniques comprise of graphitization in the furnace which entails hours of heating in an atmosphere of inert gas [9,10]. Hence a new procedure which can function with the limited cost of fabrication and ease of preparation needs to be targeted on. In this regard, microwave method is a competent method which maintains a uniform temperature gradient with minimum time consumption. It is considered an energy saving method and most importantly there is no direct interaction between the reactants and energy source [11–13]. Hence microwave method has been employed in heating various solid carbon commendably. Although several other efforts to increase the graphitization were described, graphitization by microwave method has not been much explored and still requires further exploration in improving the graphitic nature, due to the fact that the degree of graphitization affects the thermal and electrical properties of the graphitic materials.

Teawon et al. [1] graphitized commercial activated carbon using microwave irradiation by metal catalyst impregnation with just 5 min of reaction time under argon atmosphere. The prepared material was examined as an anode material for lithium-ion batteries. The crystallinity of the prepared graphite by microwave irradiation was confirmed by XRD analysis, where a change in (002) peak after microwave heating was confirmed with the reference graphite powder. In our work, graphite mineral which is extensively available in Indonesia [6] is processed for upgrading graphitic nature which has colossal applications [14,15]. The graphitization of the natural graphite is enhanced in the present study, unlike other reported work where synthetic graphite from carbon precursors was used. This could be the preliminary footprint for processing of graphite from its ore. Materials prepared from minerals and from waste can be effectively used for the synthesis of materials with a wide range of applications such as adsorption, photocatalysts, an electrode for supercapacitors [16] etc.

Here, we report microwave irradiation for graphitization with the aid of catalyst for processing graphite mineral resource obtained from Indonesia [6]. The graphite mineral resource was subjected to leaching with hydrofluoric acid and the resulting material was treated with different metal salt catalysts followed by microwave graphitization for various reaction time. The graphitized materials prepared with different metal catalysts were subjected to XRD and Raman analyses to reveal more information about the nature of graphitization. The mechanism underlying the formation of crystalline graphite with high extent of graphitization was also attempted. This work will reveal a new perspective for the preparation of graphite from the extensively available graphite mineral resources in Indonesia. It was observed that the crystallinity of the graphite is a vital aspect to make it to commercial standards. As a precursor for the preparation of graphene and graphene oxide, the main goal is to improve the crystallinity of the graphite. From the commercial aspect, efforts have been made for the preparation of GO from the graphitized carbon prepared by microwave irradiation using the nickel sulfate catalyst. The XRD results of GO prepared and the GO obtained from commercial graphite were compared and the results are on par with each other.

2. Experimental

2.1. Chemicals

Nickel sulfate hexahydrate ($NiSO_4{\cdot}H_2O$), iron nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$), chromium nitrate nonahydrate ($Cr(NO_3)_3{\cdot}9H_2O$), cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), and hydrofluoric acid (HF) were obtained from Merck Chemicals and used without further purification.

2.2. Graphitization using metal salts as catalyst

In our previous work graphite was separated from its ore by froth flotation process from other gangue minerals and the recovery of graphite was about 70% [6]. It is leached using hydrofluoric acid (HF) in the ratio 1:5 to obtain graphite with almost 98% purity. In the processing of graphite from its mineral, about 10 g of the sample is treated with 30% HF in the ratio 1:5 for 2 h to make the dissolution of soluble minerals. The mixture is then heated for 2 h at 80 °C under constant stirring. The residue was filtered and repeatedly washed with distilled water until neutral pH and dried at 80 °C overnight. The dried powder thus obtained is analysed for any impurities using XRF analysis and the absence of fluoride in the processed sample was also ascertained. The method used for the preparation of graphite with 94% purity from its mineral is described in our previous work [8].

Graphitization of the carbon experimented with the aid of four different metal salt catalysts such as nickel sulfate, iron nitrate, cobalt nitrate, chromium nitrate using microwave method. 100 mL of 6 mmol concentration of metal salt solutions was prepared and mixed separately with 1 g of graphite and stirred for 4 h. The mixture is heated at 75 °C for 24 h and the mixture is cooled to room temperature, filtered and dried in an oven at 60 °C for 5 h. The dried powder of graphite is subjected to microwave irradiation for 5 min, 10 min and 20 min of reaction time respectively with the purging of inert argon gas at a flow rate of 1 L/min. The samples after the microwave treatment are collected separately and characterized by various techniques.

2.3. Characterization

The microwave graphitization of the material is experimented using Microwave Oven (IEC 60705) with 1000 W capacity, 220 V and a microwave frequency of 2450 MHz which was customized with inlet and outlet valve for passing Inert gas such as Argon. X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (pan-analytical X'pert PRO series PVV 3040/XO with $\lambda = 1.5418$ Å) made in the Netherlands. X-ray Fluorescence (XRF) analysis was done using XRF Rigaku NEX CG to analyse the purity of the materials. Scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDAX) analysis was performed using Su 3500-EDAX Hitachi, and EDAX Apollo X. Prior to the analysis, the materials were sputtered with 2.5 nm gold thickness. Raman spectra were recorded at room temperature using Raman spectrometer (XploRA One) from Horiba Scientific using argon ion laser source with an excitation wavelength of 523 nm.

3. Results and discussion

3.1. XRD analysis

XRD patterns of crude graphite before and after leaching is shown in the Fig. 1. The XRD pattern of graphite after leaching illustrates a sharp peak at a 2Θ value of 26.67° peak corresponding to (002) plane of graphite which has been shifted from 25.89°. This clearly justifies the graphitization of amorphous material into a crystalline material after the leaching process [4,9,17]. The shift in the peak to a greater diffraction angle with strident intensity suggests a proliferation of the graphite thickness and diminution in the interlayer spacing of *d* (002) plane. Apart from the graphitic peak, a peak at 54.8° analogous to (004) plane is sharper (as marked in Fig. 1) after leaching compared to the peak at 54.2° in graphite before leaching, validating a better crystallinity in the leached material. The inset of Fig. 1 shows a vibrant glimpse of an enhanced crystallinity in the material before and after leaching.

Different metal salts such as nickel sulfate, iron nitrate, cobalt