Physical Properties Comparison of rGO-like Phase Prepared from Coconut Shell and the Commercial Product

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Abstract: Electrical and magnetic properties of graphene-derivatives materials are strongly influenced by their physical properties. Here we report a study on physical properties of reduced graphene oxide (rGO) prepared from two different raw materials, namely coconut shell (rGO-s) and graphite mineral (rGO-c, produced by Graphenea Inc.). rGO-s was prepared by carbonization method followed by mechanical exfoliation. While both samples have the same density of about 1.9 g/cm³, rGO-c has more porous compared to rGO-s. Specific surface area in rGO-c was also obtained much larger than that of rGO-s. Examinations on particle size and surface morphology show that rGO-c has homogenous particles which consist of transparent thin sheets, while rGO-s has rather heterogeneous particles that look like dense stacked sheets. The presence of C and O was confirmed at the observed morphology. The difference in physical features was found to influence the obtained electrical conductivity of the samples. rGO-c has higher conductivity than rGO-s. Estimation on gap energy (E_g) indicates that rGO-c and rGO-s have E_g in the range of semiconducting materials. The study provides a better understanding on physical properties of coconut shell-derived rGO to further revise synthesis method to improve quality of the obtained rGO.

Keywords: coconut shell; density; porosity; reduced graphene oxide.

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I. INTRODUCTION

Carbon compounds derived from biomass have become potential alternatives to minimize the use of unrenewable mining coals in many industrial applications. Because of its orbital hybridization and bonding nature, carbon has several allotropes that have different physical properties. Graphene, fullerences and carbon nanotube (CNT) are carbon’s allotropes with sp² hybridization, while diamond is the allotrope with sp³ hybridization [1]. One of the graphene derivatives that has mixed sp²/sp³ hybridization is reduced graphene oxide (rGO). rGO has a graphitic structure as that of graphene with some defects, oxygen, and hydrogen on its sheet [2,3]. Thus, rGO can have a wide range of properties which in some cases yield better performance as a chemical sensor [4,5], supercapacitor [6-8], hydrogen storage [9], photovoltaic cells [10,11], and so on. rGO has been prepared from natural resources using several methods including carbonization, pyrolysis and hydrothermal [12-15]. Natural resources provide a new insight to synthesize carbon-based compounds which is environmentally friendly without exploiting mining materials. However, the challenge is that the obtained carbon materials tend to have poor porous structure and vague morphology. Therefore, study on physical properties of the compounds is the key to improve synthesize method applied. It is also necessary as a base to discuss the observed magnetic and electrical properties of the obtained materials.

The biomass of coconut shells is rich in carbon which is about 70% of the total elements [16]. It also has high hardness and exhibits high volatility and low ash content [17], thus carbon compound derived from coconut shell is expected to bring in the high specific surface area [18]. Moreover, coconut shell is relatively easy to be found as Indonesia is the third-largest producer of coconut in the world [19]. In the present study, we prepared the rGO-like phase from a coconut shell. Physical properties of the synthesized rGO (rGO-s) were then compared to those of the commercial rGO (rGO-c) which was prepared from graphite. Variation in physical properties is expected to differ in the observed magnetic and electrical properties. Thus, we also examined the electrical conductivity of the samples. Despite rGO-c has a better porous structure, defined morphology and higher specific surface area than rGO-s, both samples possess the same density, and their gap energy was found to be in the range of semiconducting compounds. Results in this study provide a better understanding of the physical properties of coconut shell-derived rGO to further revise the synthesis method applied to produce rGO with good quality.
II. EXPERIMENTAL METHODS

The commercial product of rGO (rGO-c) was bought from Graphenea Inc. It was prepared from graphite by the modified Hummer method. Chemical and thermal reduction processes were applied to form rGO from graphite oxide [2, 3]. The synthesized rGO (rGO-c), on the other hand, was prepared from biomass of coconut shell by the carbonization method [21, 23]. The old coconut shell was cleaned by removing husks adhered on its surface. The cleaned shell was carbonized yield in charcoal flakes which were then grounded and sieved to get homogeneous charcoal powders. Furthermore, the powders were sonically exfoliated in the medium of distilled water to form a thinner graphitic layer. Physical properties of the samples, rGO-c, and rGO-s were then examined. Brunauer-Emmett-Teller (BET) theory was applied to identify porosity and to measure the specific surface area of the samples. The measurement was carried out using Quantachrome Instruments Nova 1200e Surface Area & Pore Size Analyzer. The density of the powders was analyzed using a pycnometer. Particle size analyzer (PSA, Zetasizer Nano ZS Malvern) was used to examine particle size distribution of the powders in distilled water. The surface microstructure and its elemental distribution of the powders were also checked using a Scanning Electron Microscope (SEM) with Energy Dispersive X-ray (EDX) spectroscopy. To estimate the gap energy of the samples, optical spectra obtained by the Uv-Vis spectrophotometer (Genesys 10S) in the wavelength range of 200-800 nm were analyzed using the Tauc Plot method [20]. The electrical conductivity of the samples was determined from V-I data obtained by a four-point probe method.

III. RESULTS AND DISCUSSION

Analyses on phase and functional groups presented in the samples have been reported in [22, 23]. Two broad peaks at 2θ of about 24° and 43° were observed in XRD patterns of the samples, indicating the presence of the rGO-like phase. Spectra of Fourier Transform Infrared (FTIR) also confirmed that both samples have similar functional groups of C=C, C=O, C-O, C-H, and O-H. However, qualitative analysis of the spectra suggested that rGO-s has a higher percentage of oxygen functionality, which is twice as large as that of rGO-c [23].

Table I summarizes porous characteristics, specific surface area and density of the samples in the powder form. The density of both samples was found to be quite similar, which is 1.91 and 1.95 g/cm³ for rGO-c and rGO-s, respectively. The volume and diameter of porous presented in rGO-c are much larger compared with that of rGO-s. rGO-c has approximately 1.29 cc/g porous with a diameter of 10.82 nm, while rGO-s has about 0.18 cc/g porous with a diameter of 2.44 nm. These porous features will directly affect the specific surface area of the samples. The more porous presented in the sample, the larger the surface area will be obtained. rGO-c and rGO-s have a specific surface area of approximately 475 m²/g and 298 m²/g, respectively. Characteristics of large porous and high specific-surface-area are essential in carbon-based materials for their potential applications.

The specific surface area is related to the particle size of the samples. Small particles tend to have a large specific surface area, and vice versa, large particles have a small surface area. Fig. 1 illustrates the particle size distribution of rGO-c and rGO-s examined by PSA. A single peak at 200 nm was observed in rGO-c. This indicates that rGO-c has homogeneous particle-size-distribution. It also implies that the morphology of rGO-c is like thin sheets, thus no other peak signifying a thickness of the sheets can be seen. In the case of rGO-s, two broad peaks are observed at 105 nm and 615 nm in the distribution spectrum. It suggests that the particle-size distribution of rGO-s is not quite homogeneous. A small peak at 105 nm might indicate the thickness of the particle, and a high peak at 615 nm could be related to a cross-sectional area of the particle. To confirm these suggestions, the surface morphology of
FIG. 2: Surface morphology of (a). rGO-s and (b). rGO-c observed by Scanning Electron Microscope (SEM). Inset in (a) is the close view of a spot in the image.

FIG. 3: Optical absorbance spectra of rGO-c and rGO-s obtained from UV-Vis spectroscopy.

| Element   | rGO-s (wt%) | rGO-c (wt%) | rGO-s (at%) | rGO-c (at%) |
|-----------|-------------|-------------|-------------|-------------|
| Carbon (C)| 78.4        | 74.4        | 83.1        | 79.5        |
| Oxygen (O)| 20.8        | 25.6        | 16.6        | 20.5        |
| Potassium (K) | 0.8  | -           | 0.3         | -           |

However, this element can be eliminated by heating process and/or dissolution in acid. Thus, a thermal reduction is necessary to prepare a rGO-like phase from biomass in addition to mechanical exfoliation.

The physical features of the samples influence their electrical and magnetic properties. Our previous studies reported that magnetization of the rGO-like phase synthesized from coconut shell strongly depends on defects [22,23]. The magnetization enhances when the concentration of defect increases, and this can be tuned by controlling temperature applied in the thermal reduction process [22]. The saturation magnetization of rGO-s is larger than that in rGO-c as rGO-s has more defects compared with rGO-c [23]. In this case, a contribution from magnetic impurities has been subtracted. Here, electrical conductivity ($\sigma$) of rGO-c was found to be one order larger than that of rGO-s, in which $\sigma$ is about 28 S/m and 4 S/m for rGO-c and rGO-s, respectively. By evaluating $\sigma$ at the elevated temperature between $30^\circ$C and $100^\circ$C with $10^\circ$C step, we found that gap energy is approximately 0.30 eV for both samples. Furthermore, gap energy was also examined from optical absorption spectra measured by UV-Vis spectrometer.

Fig. 3 displays the absorption spectra of rGO-c and rGO-s solution with the same concentration within the wavelength range of 200-800 nm. The first edge peak at ~230 nm was observed in both samples. This peak indicates $\pi-\pi^*$ electron transition of aromatic C-C. Maximum absorption occurs at the same wavelength of 290 nm in the samples. This peak implies...
the presence of n-π* transition originated from C=O. By applying the Tauc Plot method [20], plot of photon energy (in eV) and (αhν)2 (in eV cm−1)ν, gap energy was estimated to be 0.31 eV and 0.37 eV for rGO-s and rGO-c, respectively. These values agree with those calculated from V-I data and are in the range of gap energy of semiconducting materials. It indicates that the obtained rGO-like phase can be potentially applied in technologies required semiconductor compounds, such as solar cell.

IV. SUMMARY

Investigation on physical properties has been done on reduced graphene oxide (rGO)-like phase prepared from biomass of coconut shell (rGO-s) and the commercial product (rGO-c). The density of rGO-c and rGO-s was found to be ~1.9 g/cm3. Analysis of porous characteristics shows that rGO-c has more porosity of about 1.3 cc/g with a diameter of 10.8 nm compared to rGO-s which has 0.2 cc/g porous with a diameter of 2.4 nm. The specific surface area in rGO-c was also obtained much larger than that of rGO-s. rGO-c and rGO-s have a specific surface area of ~298 m2/g and ~475 m2/g, respectively. Examinations on particle size and surface morphology show that rGO-c has homogenous particles which consist of transparent thin sheets, while rGO-s has rather heterogeneous particles that look like dens stacked sheets. Moreover, the presence of C and O was confirmed at the observed morphology. These physical features were then found to influence the obtained electrical conductivity of the samples. rGO-c has higher conductivity than rGO-s. Estimation on gap energy (Eg) from both data, electrical conductivity, and optical absorption spectra, indicates that rGO-c and rGO-s have Eg in the range of semiconducting materials. To enhance the porous and specific surface area, thermal reduction followed by chemical and mechanical exfoliations is suggested to prepare rGO from coconut shell.

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