Structural Analysis on Reduced Graphene Oxide Prepared from Old Coconut Shell by Synchrotron X-Ray Scattering

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ABSTRACT. This work is aimed to identify the distribution of size and structure of the reduced graphene oxide (rGO) particles before and after the mechanical exfoliation process from coconut shell. The burnt sample was heated at 400°C in ambient air, followed by sonication and centrifugation method for various concentration. The characterization were performed by using wide angle X-ray scattering (WAXS) and synchrotron small angle X-ray scattering (SAXS). Based on SAXS result, the structure of rGO showed that in low range of momentum transfer (Q), the particle size was too big to be measured using SAXS. In the high Q, the graph shown the apparent absence of change in curvature which indicates that the small particles are typically seen on high Q range, having aggregate with a new shape and big particles. The average fitting slope is -3.3, implying that the particles structure tends to be fractal (rough) surface, where the particles form aggregates to become bigger size and irregular structure. Further, the WAXS characterization shows that the exfoliation step has not affected the rGO phase formed.

1. Introduction
Graphene is a burgeoning material with a honeycomb-like two dimensional crystal structure formed by carbon atoms in $sp^2$ hybrid junction, exhibits incomparable electronic, thermal and mechanical properties [1]. The most important issue to realize the potential of graphene is to achieve its mass and controllable production [2]. There have different names of graphene, such as chemically modified graphene, functionalized graphene, chemically converted graphene or simply graphene. Reduced graphene oxide (rGO) is a promising material for many applications such as in the development of energy-storage capacitors, field effect transistors sensor etc [4].

Separation of thin layers of graphene (a 2D material) from a 3D layered bulk graphite results in an increase of its electrical conductivity. Graphite is an available in large quantities from natural sources and consists of a stack of flat graphene shets standing together by weak Van der Waals forces. The carbon atom plane in graphite oxide is heavily decorated by oxygen-containing groups, which expand the interlayer distance and make the atomic thick layers hydrophilic. These oxidized layers can be exfoliated in water under moderated ultrasonication [4]. This sonication produces a thinner layer of rGO.

The polydispersity of nanoparticles is of importance in controlling properties related to their small size and high specific surface area. Current techniques for the determination of particle size...
distribution on nanoscale can be categorized into some measurements, such as small angle X-ray scattering (SAXS). The determination of primary particle size distributions for nanoparticles that are aggregated into mass-fractal structures is challenging due to the overlap of structural features [5]. The SAXS is a well established technique, long used for colloidal system and later polymers, which has seen a resurgence because of the availability of high intensity synchrotron sources and the current trend towards the investigation and application of nanoscale structures [6].

In the previous research, it has been conducted characterization of an old coconut shell charcoal treated with heating at a certain temperature and atmosphere and found that there was a phase of reduced graphene oxide based on XRD graph pattern. Besides that, the width of the band gap energy in the overall of coconut shell charcoal were in the range of 0.07 – 0.67 eV which was still included in the range of reduced graphene oxide material. As we know that reduced graphene oxide is a semiconductor material, so it is strongly support that reduced graphene oxide can be made from an old coconut shell charcoal [7].

However, from the previous research it is not yet known how the shape, particle size and the distribution of the particle are in the form of powder and solution of an old coconut shell charcoal. So, this research focuses on the identification the shape, particle size and the distribution of the particle of rGO synthesized from the old coconut shell charcoal after getting an exfoliation and heating treatment using synchrotron SAXS and wide angel X-ray scattering (WAXS).

2. Experiment

The materials used in this study are an old coconut shell powder, and distilled water. The equipment used in this study are mortar, pestle mortar, crucible, sandpaper, furnace tube, drilling machine, ultrasonic cleaner, centrifuge, beaker glass, digital balance, cutter, spatula, aluminum foil, and rubber hoses. Sample preparation was done by cleaning the old coconut shell using sandpaper. It was burnt on fire until it turns into charcoal. The resulted and selected charcoal was then heated at oven overnight at temperature of 150ºC to remove water content. It was smoothed using the pestle mortar to form the coarse powder and using mortar to form the smooth powder and sieve using 500 mesh. Furthermore, it was heated using tube furnace at temperature 400ºC for 3 hours in ambient air. Then, the aqueous solution of rGO was prepared by dispersing 10, 15 and 20 mg charcoal powder into 100 ml of distilled water by ultrasonic cleaner for 45 minutes and deposited by centrifuge for 15 minutes. Then, the precipitate in the solution was dried to be used in the form of powder. The samples were characterized using XRD, WAXS and SAXS to identify the structure, shape and particle size distribution.

3. Results and Discussion

SAXS measurements were carried out on beamline number 1.3 at Siam Photon Laboratory of Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand, to observe the particle size distribution, structural dimensions and shape of coconut shell charcoal which form the structure of rGO. The SAXS instrument provides nondestructive measurement and is able to measure the actual size of particles, distribution, shape, dimensions because the X-ray radiation from the instrument can be directly transmitted and scattered to the sample [8].

The intensity of the SAXS was generated by 9keV of X-Ray energy which is presented as a function of the scattering vector (q). Scattering vector is defined as $(4\pi/\lambda)\sin(\theta/2)$, where $\lambda$ and $\theta$ are the wavelength of X-Ray and scattering angle of SAXS. The measurement used a CCD detector and 3.2 meter of sample to detector (SDD). The material standard that used during the measurement was Block Co-polymer (SEBS). Data result was analyzed by using the SAXSIT and SASfit software. The sample that used was in the form of powder and solution.
Figure 1. The SAXS pattern of rGO sample heated at 400°C in a) solution sample, b) powder sample.

Figure 2. The SAXS graph and fitting slope of powder and solution.

Figure 3. The XRD and WAXS patterns of the sample heated at 400°C.
The SAXS result in Figure 1 showed that pattern of all type of samples have no black circular line in the middle of the pattern. Analysis of data reduction for the pattern was carried out by 4 steps: (i) read the pattern, (ii) align the pattern, (iii) subtract the background, and (iv) calculate SAXS profile I(q). Water was used as the background for the sample. The pattern indicates that the structure of the rGO is in the form of amorphous carbon structure and composed of random layers. These amorphous and random layers caused by the precursor material that used as a sample. An old coconut shell charcoal composed of cellulose, hemicellulose, lignin and a lot of metal substances from nature that form the amorphous structure.

The SAXS data for both type of samples, powder and solution, in Figure 2 show that the particle size of rGO in low range of momentum transfer (Q) is too big to be measured using SAXS. In the high range of Q, it shows the apparent absence of change in curvature which indicates that the small particles are typically seen on high Q range, having aggregate with a sphere shape and big particles. The big size of particles related to the exfoliation process during the experiment. Exfoliation process used to break down the van der waals bonding between the rGO layers to become thinner. This molecule bonding forces is weaker than covalent bonds such as the single or double bonding between carbon atoms that form a hexagonal structure. Energy vibration generated by the ultrasonic cleaner and the length of time (45 minutes) used in the process of exfoliation is not enough to make the oxygen, hydrogen and carbon bond between the rGO layers split together that produce particle size with extensive surface and thick layer. The average fitting slope in Figure 3 for powder and solution sample is -3.2, implying that the particles structure tends to be fractal (rough) surface (3<Δ≤4), where this value revealed that rGO was a three-dimensional structure with a fractally rough surface [9]. This fractal surface comes from the aggregation of some particles that is caused by low dispersion of the solution and also affected by exfoliation process. Furthermore, the slope value indicates that the dimension of the particles is in the form of 3D with a fractal surface because it still has a big size of particle of rGO. This simply exfoliation technique still not enough to exfoliate the layers of rGO and change the particle dimension of rGO from 3D of sphere become 2D.

The WAXS measurement was conducted using a CCD detector, 89 cm distance of sample to detector (SDD), and the standard material of 4-Bromobenzoic Acid. The WAXS pattern in Figure 4 for all samples shows a similar pattern of the XRD data, consisting of two broad peaks which are located at 2θ = ~ 23⁰ and ~ 43⁰. In rGO, the carbon 002 peak is present at 2θ = ~ 23⁰ and 100 peak is present at 2θ = ~ 43⁰. The WAXS characterization shows that the exfoliation step has not affected the rGO phase formed. A shift that occurs at the angle of 43⁰ due to difference in wavelength between WAXS of 1.38 Å and XRD of λ = 1.54 Å (Cu-Kα). Comparing to XRD with WAXS patterns, one may identify that there is a same phase in the sample as rGO. The broad peak corresponding to an amorphous structure is possibly a pile of random arrangement of thick parallel layers. The broad peak at 2θ = ~ 23 and 43⁰ represent that the hkl of rGO are (002) and (100), respectively. The carbon layers are bound in the c-direction by weak van der waals forces [8].

Using Bragg equation, the inter-layer spacing and lattice parameter (a and c) of rGO can be measured. Comparing the calculation result of inter-layer spacing (d) of rGO from old coconut shell between XRD and WAXS, is indicated at 2θ = ~ 23 to be 4.03Å, at 2θ = ~43⁰ to be 2.10 Å by XRD and at 2θ = ~ 23 to be 3.61 Å, at 2θ = ~43⁰ to be 2.01 Å by WAXS. The lattice parameter at hkl (002) and (100) of WAXS (λ = 1.38 Å) and XRD (λ = 1.54 Å) are c = 7,232 Å, a = 1,640 Å and c = 8,071 Å, a = 1,673 Å, respectively. Based on literature by Rajaura et al, most intense peak in the pristine graphite is appearing at 2θ = 26,6⁰ which is corresponding to (002) plane of graphite and inter-layer spacing is about 3.39 Å. After chemical reduction by hydrogen, a new broad peak is appearing at 2θ = 23,72⁰ which corresponds to inter-layer spacing of 3.85 Å. This is attributed to the removal of functional group and moisture of oxygen and hydrogen [10]. The similarity of d inter-layer spacing between rGO from old coconut shell and reference confirm that WAXS and XRD measurement form a rGO phase. Bigger value of inter-layer spacing and lattice parameter between measurement and common reference caused by the oxygen, hydrogen and impurity that bonded in hexagonal carbon structure of rGO. Inter-
layer spacing and lattice parameter at hkl (002) and (100) between WAXS and XRD, shows that there is a small shift due to the differences of wavelength.

4. Conclusion
The structure of rGO in low Q range describes that the particle size is too big to be measured using SAXS, while in the high Q range, the apparent absence of change in curvature indicates that the small particles develop aggregate with a new shape and bigger particles. The average fitting slope of -3.2 implies that the particles structure tends to be fractal (rough) surface (3 < D ≤ 4), where this value revealed that rGO was a three-dimensional structure with a fractal rough surface due to the aggregation and exfoliation. The WAXS pattern for all samples were similar to the XRD data, featuring two peaks belonging to rGO phase. The similarity of d inter-layer spacing and lattice parameter between rGO from old coconut shell and reference confirm that WAXS and XRD measurement form a rGO phase. Inter-layer spacing and lattice parameter at hkl (002) and (100) between WAXS and XRD, shows that there is a small shift of c-axis due to the differences of wavelength.

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