CHAPTER 5 CONCLUSIONS

In this work, physical and chemical properties of nanographite prepared by sonication technique were studied. Effect of different sonication times, including 3, 6, 12, 36, and 72 hours, on thickness of nanographite were reported. Graphene oxide and reduced graphene oxide were prepared by Hummers'method. Thin film made from self-assembly of nanographite and reduced graphene oxide sheets can be used as active layer for pH sensor. The resistance of the sensor changed when contacted with liquid of different pH values.

5.1 Nanographite

We demonstrated that nanographites can be exfoliated from graphite without any assistance from chemicals and hazardous materials. Only distilled water was enough to do this. Sonication is a powerful technique for synthesizing nanographites. The color of the suspension became darker for longer time of sonication becauselonger time of sonication enhanced the concentration of exfoliated nanographite . Sonication time strongly affected the homogeneity and stability of nanographite suspensions. Stably-dispersed suspensions were obtained from 36 and 72 hours of sonication time, representing a clear gray suspension for more than 3 months as confirmed by UV-Vis absorption spectra.

AFM height profile, SEM and TEM indicated that bulk graphite was almost broken and exfoliated and became nanographite. The thickness of nanographite was less than 5 nm. The calculated result implied that most of them were less than 15 layers of single layer graphene. Raman spectra showed that the G-band was at about 1577-1581 cm^{-1} which is from the stretching vibration of any pair of sp^2 sites, whether in C=C chains. The D band was at about 1350 – 1354 cm^{-1} which is the breathing mode of those sp^2 sites only in rings, not in chains. The increase of the peak intensity in the D band of nanographite (72 hour sonication) might come from the increasing of the sp^3 atom and the disordered structure of graphite. The 2D band peak of raw graphite changed from 2725 cm^{-1} to 2703 cm^{-1} after 72 hour of sonication, which might correspond to the exfoliation of nanographite.

5.2 Reduced graphene oxide

The color change from yellow brown of graphene oxide suspension to black of reduced graphene oxide suspension was seen clearly due to reduction process, which is probably a result of an increase in the hydrophobicity of graphene oxide sheets caused by a eliminate oxide functional group out of graphene oxide sheets or a decrease in polar functionality on the surface of graphene oxide sheets. TEM image of graphene oxide which obtained from Hummers' method indicated that we obtain graphene oxide after treating graphite with strong oxidizers and dispersion in basic solutions to yield monomolecular sheets or graphene oxide which is the single-layer form of graphite oxide. There are plenty of graphene oxides stacked on the graphite oxide. The crumpled structure of the graphene oxide exhibited maybe due to the multiplicity of oxygen functionalities in thin GO layers. TEM image indicated that the reduced graphene oxide as well as graphene oxide has the tendency to scroll and wrinkle.

Raman spectram of raw graphite and reduced graphene oxide contained both G and D bands at 1590 and 1351 cm^{-1} respectively. This result indicated that the reduction started from the edges of graphene oxide particles and proceeded into the basal planes. During the reduction, parts of the basal planes near the edges became reduced and subsequently snapped together due to π–π interactions, thus narrowing the interlayer distance.

5.3 Characterization of nanographite and reduced graphene oxide-based pH sensor

Assembly of nanographite and reduced graphene oxide sheets as a film can be used as pH sensor. pH sensors made from nanographite and reduced graphene oxide showed that the resistance of the devices decreased linearly with increasing pH values in the range of 1-14.

The sensing mechanism of nanographite (device A) and reduced graphene oxide (device B) can be explained by the hydroxonium ions (H_3O^+) and hydroxyl ions (OH^-) adsorbed on surface of nanographite and reduced graphene oxide. The absorbed ions in an acid and a base are H_3O^+ and OH^-, respectively. Both ions adsorption mechanisms are nonfaradaic or capacitive in which the charges cannot transmit across nanographite and reduced graphene oxide. The ability of charge storing of nanographite and reduced graphene oxide surface caused the reduction of the resistance.

The n-doping and p-doping of nanographite and reduced graphene oxide make by hydroxonium ions (H_3O^+) and hydroxyl ions (OH^-), respectively. The arrangement of hydroxyl ions (OH^-) in the inner Helmholtz region is more ordered than hydroxonium ions (H_3O^+). Therefore, the resistances of the sensor decrease with increasing pH values in the range of 1-14.

The sensitivity of device A and B is 220 kΩ pH^{-1} and 2.30 kΩ pH^{-1}, respectively. These results indicate that device A is more sensitive in the detection than device B because the sensitivity value of device A is more than the sensitivity of device B. The pH resolutions of device A are 0.32 and 0.16 pH in acid and base, respectively. For device B, the pH resolution is 0.42 and 0.41 pH in acid and base, respectively. These results indicate that a change of pH resolution is reflected in the sensing mechanism when pH changes from acid to base which caused the arrangement in the inner Helmholtz region is more ordered. The sensing trend of device A and B is same because both of devices showed that the resistance of the sensors changes upon doping with liquids of different pH, demonstrating a linear resistance-pH relationship.

5.4 Future works

Although thin films prepared from self-assembly of nanographite and reduced graphene oxide sheets can be used as pH sensor in which the resistance of the devices decreases with increasing pH values, the sensitivity of the these sensors still low. Therefore, the quality and sensitivity of these devices can be further improved by adjusting the synthesis and fabrication of sensor device. The following works are recommended as a follow up to this study:

1. Improved synthesis of nanographite and graphene using another method such as chemical vapor deposition (CVD), improved Hummers' method and Hummers' method with additional $KMnO_4$.
2. Improved properties of nanographite and graphene by adding nanoparticle or carbon nanotube.
3. Improved fabrication of sensor device with reduction size of electrodes and body of sensor.
4. More measurement on the resistance changing with chemicals in food such as pH changing in food, pesticide and protein changing in food.