CHAPTER 3 EXPERIMENTAL

In this chapter, the procedures of preparation and characterization of nanographite by sonication and reduced graphene oxide by Hummers' method and reflux will be explained in details. pH sensor made from self-assembly of nanographite and reduced graphene oxide sheets as a thin film will be compared and described.

3.1 Material

1. Bulk graphite (POCO, 99.999%)
2. Graphite flakes
3. Sodium nitrate ($NaNO_3$, Ajax Finechem Pty Ltd.)
4. Potassium permanganate ($KMnO_4$, Ajax Finechem Pty Ltd.)
5. Distilled water
6. Deionized water (RCI Labscan Limited)
7. Sulfuric acid (H_2SO_4)
8. Hydrogen peroxide (H_2O_2, Merck Schuchardt OHG)
9. Hydrazine hydrate (H_6N_2O, RFCL Limited)
10. pH buffer (1-14)

3.2 Equipment

1. Cylinder
2. Erlenmeyer flask
3. Round bottom flask
4. Condenser
5. Mortar
6. Pestle
7. Silicon Wafer
8. Glass slide
9. Micropipette
10. pH meter (Lutron, PH-222)
11. Thermometer
12. Filter paper
13. Ice bath
14. Analytical Balance (Sartorius ED224S)
15. Digital multimeter (FLUKE 17B)
16. Hot plate magnetic stirrer (Stuart CB162, LMS HTS-1003)
17. Fritted glass funnel
18. Buchner funnel
19. Hood
20. Even (Froilabo)

21. Vacuum pump
22. Ultrasonic bath (Elmasonic E100H)
23. Sputter Coating Deposition (SC 7620)
24. Scanning Electron Microscopy (SEM, Hitachi S-4700)
25. UV-Visible Spectroscopy (Jasco V570)
26. Raman Spectroscopy (Renishaw inVia)
27. Atomic Force Microscopy (AFM, Veeco Scanning Probe MicroScope: NanoScope IV)
28. Transmission Electron Microscopy (TEM, HU-12A)

3.3 Preparation and characterization of nanographite

Bulk graphite (99.999%) obtained from POCO was used as a starting material for preparing nanographite. 0.5 g of bulk graphite was first ground with a mortar and pestle and, then, added to 500 mL of distilled water. The suspension was sonicated in an ultrasonic bath, 20 kHz. Effect of sonication time on nanographite exfoliation was studied. The sonication times included 3, 6, 12, 36, and 72 hours.

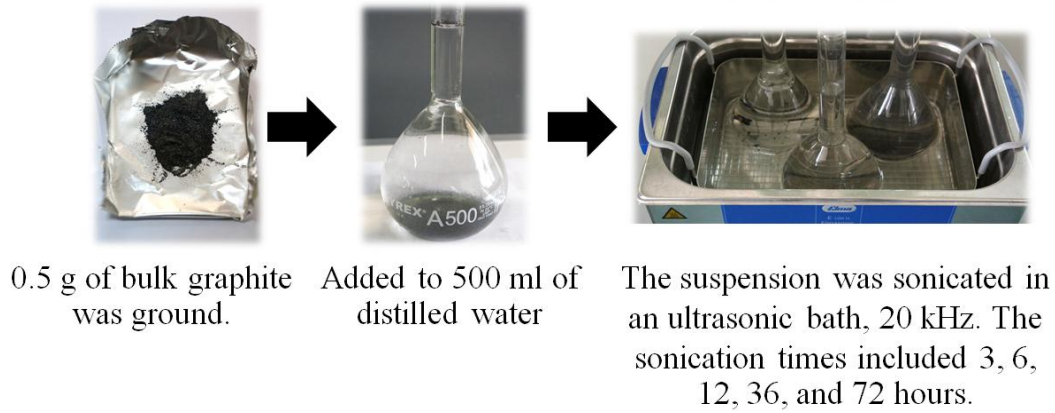

Figure 3.1 Preparation of nanographite

The morphological features and thickness of nanographite were investigated by scanning electron microscopy (SEM), atomic force microscopy (AFM) and transmission electron microscopy (TEM). The graphitic characteristics of the exfoliated nanographite were characterized using UV-visible spectroscopy and Raman spectroscopy with an excitation wavelength of 514 nm.

All of the samples for SEM were prepared by drop-casting deposition of the dispersion on silicon surface and dried in air. The samples for AFM investigation were prepared on silicon wafer and dried at the temperature of 75^{o}C. The samples for TEM investigation were prepared on copper grid. Raman spectroscopy investigations were prepared by drop-casting deposition of the dispersion on gold surface and dried at the temperature of 75^{o}C. The self-assembly of nanographite was dropped on gold surface, dried at the temperature of 75^{o}C and investigated by SEM.

3.4 Preparation and characterization of reduced graphene oxide

3.4.1 Synthesis of graphene oxide

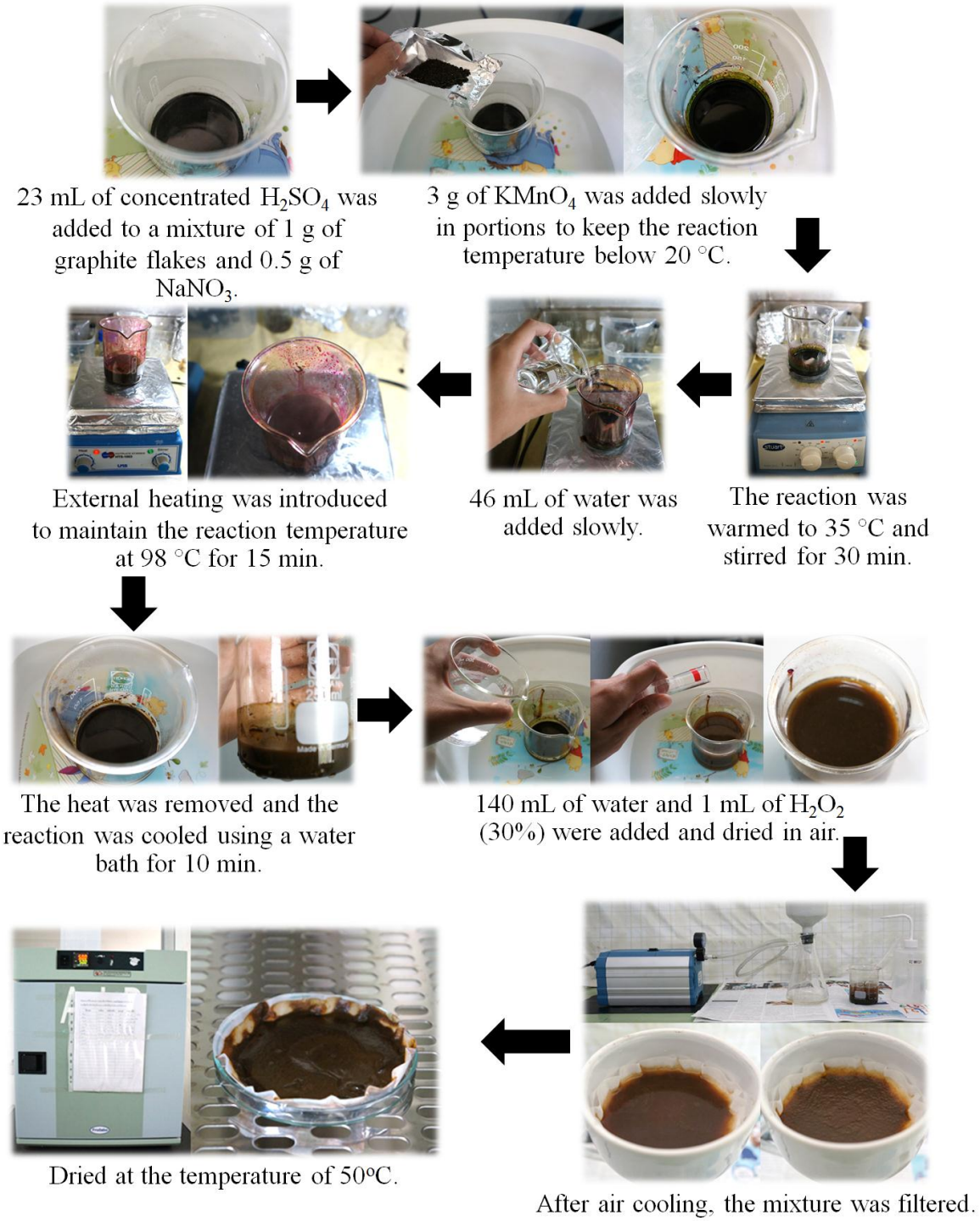

Figure 3.2 Synthesis of graphene oxide

Graphene oxide was prepared by Hummers' method [32]. 23 mL of concentrated H_2SO_4 was added to a mixture of 1 g of graphite flakes and 0.5 g of $NaNO_3$, and the mixture was cooled to 0 °C. 3 g of $KMnO_4$ was added slowly in portions to keep the reaction temperature below 20 °C. The reaction was warmed to 35 °C and stirred for 30 minutes,

at which time 46 mL of water was added slowly, producing a large exotherm to 98 °C. External heating was introduced to maintain the reaction temperature at 98 °C for 15 minutes, then the heat was removed and the reaction was cooled using a water bath for 10 minutes. In addition, 140 mL of water and 1 mL of H_2O_2 (30%) were added, producing another exotherm. After air cooling, the mixture was filtered and dried at the temperature of 50^oC.

The morphological features and thickness of graphene oxide were investigated by transmission electron microscopy (TEM). The samples for TEM investigation were prepared on copper grid.

3.4.2 Reduction of exfoliated graphene oxide with hydrazine hydrate [48]

Figure 3.3 Reduction of exfoliated graphene oxide with hydrazine hydrate

0.2 g of graphene oxide was loaded in a 250 mL round bottom flask and 200 mL of deionized water was then added, yielding an inhomogeneous yellow-brown dispersion.

This dispersion was sonicated using an ultrasonic bath cleaner until it became clear with no visible particulate matter. 2 mL of hydrazine hydrate was then added and the solution heated in an oil bath at 100 °C under air-cooled condenser for 24 hour over which the reduced graphene oxide gradually precipitated out as a black solid. This product was isolated by filtration over a medium fritted glass funnel, washed copiously with deionized water (5×100 mL) and methanol (5×100 mL), and dried on the funnel under a continuous air flow.

The morphological features and thickness of reduced graphene oxide were investigated by transmission electron microscopy (TEM). The samples for TEM investigation were prepared on copper grid. Raman spectroscopy (Renishaw inVia) with an excitation wavelength of 514 nm was used for studied the graphitic characteristics of the reduced graphene oxide. The sample was prepared by drop-casting deposition of the dispersion on silicon surface and dried at the temperature of 75^{o}C.

3.5 Fabrication of the nanographite and reduced graphene oxide-based pH sensors

We studied the difference of two pH sensors that the synthesis of graphene and the fabrication of sensors were different.

The schematic of nanographite-based pH sensor (device A) is illustrated by figure 3.4. This pH sensor made from self-assembly of nanographite sheets which used 72 hour sonication time of suspension. Gold electrodes were deposited on glass substrate via sputter coating deposition (SC 7620). The sputtering time was 75 minutes. The thickness is approximately 20 µm. Nanographite suspension was dropped and dried (75°C) on the 1 mm electrode gap. These sheets assemble to form a thin film as shown in figure 3.5.

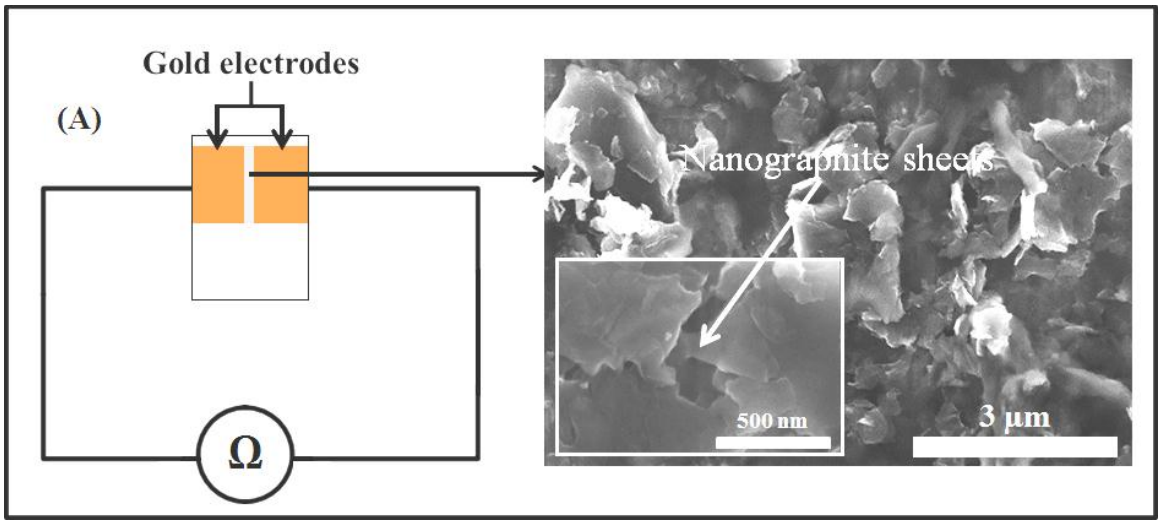

Figure 3.4 Schematic of nanographite-based pH sensor (device A)

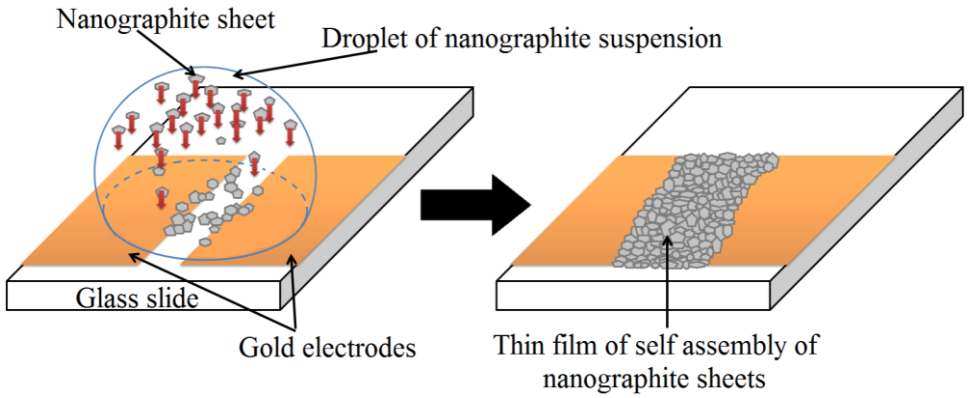

Figure 3.5 Assembly of nanographite sheets on gold electrodes

Figure 3.6 shows the schematic of reduced graphene oxide-based pH sensor (device B). The etching process used for the fabrication of gold electrodes on printed circuit board (PCB). Reduced graphene oxide suspension from Hummers' method and reflux was dropped and dried at 75°C.

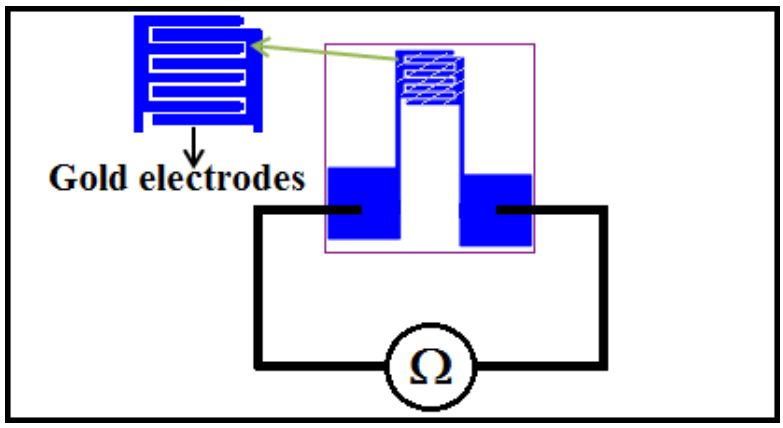

Figure 3.6 Schematic of reduced graphene oxide-based pH sensor (device B)

Figure 3.7 shows self-assembly of reduced graphene oxide sheets as a thin film. Reduced graphene oxide sheets dropped and deposited on gold electrodes. These sheets assemble to form a thin film.

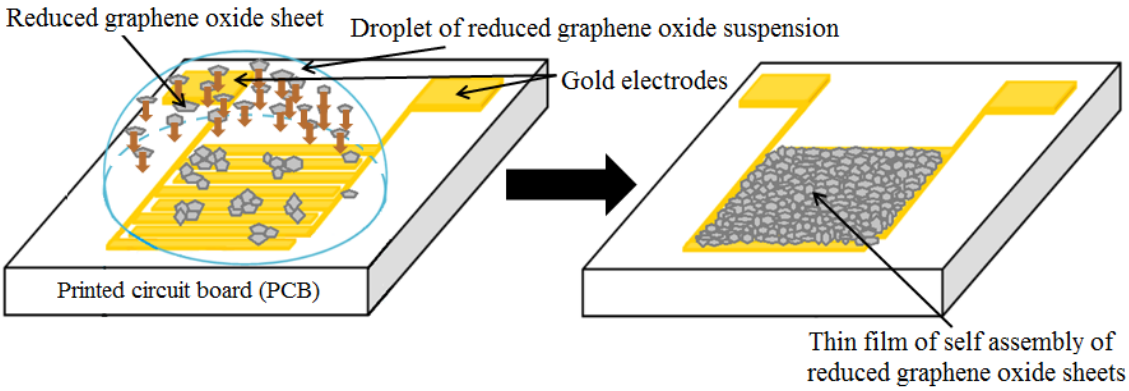

Figure 3.7 Assembly of reduced graphene oxide sheets on gold electrodes