本 科 毕 业 论 文

石墨烯/高分子复合薄膜制备及其对有机污染气体的响应研究

Preparation of Graphene/Polymer Composite Film

and Its Response to Organic Pollutants

学院名称　　<u>化学与制药工程学院</u>

专业班级　　<u>应用化学（全英语）14-1</u>

学生姓名　　　　<u>李阳</u>

导师姓名　　　　<u>迟虹</u>

2018 年　　　5 月　　　20 日

石墨烯/高分子复合薄膜制备
及其对有机污染气体的响应研究

Preparation of Graphene/Polymer Composite Film

and Response to Organic Pollutants

作 者 姓 名　　　　　　李阳

专　　　　　业　　应用化学（全英语）14-1

指导教师姓名　　　　　　迟虹

专业技术职务　　　　　　副教授

Content

Abstract

Graphene is a novel two-dimensional planar material composed of sp^2-hybridized carbon atoms. It has a large specific surface area, excellent electron mobility, good flexibility and light transmittance and strong mechanical properties. Nowadays, graphene and its composite materials have been widely used in many fields such as energy industry, environment science, nano-biomedicine, and also can be used as novel sensors. Especially in the field of chemical detection, graphene meets the design requirements of ultra-sensitive sensors with these excellent properties, and graphene composites have become popular in the field of composite materials. The oxidized graphene not only has the two-dimensional planar structure and characteristics of the graphene but also retains part of the graphene structure. After the oxidation, the graphene layers are functionalized with oxygen-containing functional groups such as hydroxyl groups, carbonyl groups, and carboxyl groups. The construction of composite materials and their simple, responsive, sensitive and selective optical sensors are of great significance to the field of chemical detection.

In this thesis, the graphene oxide was prepared by the Hummers method, graphene oxide was characterized, and a sensor capable of responding to a series of gases was prepared by combining graphene oxide with a macromolecule. The significance of this study is to open up new possibilities for further improving the sensing performance of graphene/polymer composites. In addition, it provides a new approach for the development of novel room temperature sensors.

Keywords: graphene; polymer; thin film; gas sensor

摘　要

　　石墨烯是由 sp^2 杂化的碳原子组成的新型二维平面材料，具有巨大的比表面积，优异的电子迁移能力，良好的柔韧性和透光率，强大的力学性质等优点。目前石墨稀及其复合材料已经被广泛的应用于能源、环境、纳米生物医学以及传感器等诸多领域。尤其是在化学检测领域，石墨烯以其优异的性能满足了高灵敏性传感器的设计需求，石墨烯复合材料已然成为复合材料领域的新星。经过氧化的石墨烯，不但具有石墨烯的二维平面结构和特性，保留了石墨烯的部分结构，氧化后石墨烯层间还会被插入很多羟基、羰基、羧基等含氧官能团，基于石墨稀及其复合材料构建操作简便、响应迅速、灵敏度高以及选择性好的光学传感器，对环境保护领域具有极大的意义。

　　本文针对以上背景，通过 Hummers 方法制备氧化石墨烯，对氧化石墨烯进行表征，并用氧化石墨烯与高分子结合制备可以响应一系列气体的传感器，并对传感器进行气敏测试。本研究的意义在于为进一步提高石墨烯/高分子复合材料的传感性能打开新的可能性，此外，它还为开发新型室温传感器提供了一种新途径。

关键词：石墨烯　高分子　薄膜　气体传感器

Chapter 1 Introduction

Recently, due to the rapid development of industry and agriculture, emissions of irritating, toxic and flammable volatile organic compounds (VOCs) have gradually increased, and VOCs have become one of the research hotspots in the field of environmental in recent years. Such compounds are extremely harmful to mankind and it will cause the respiratory, digestive, skin irritation and many other symptoms. It also has teratogenic, carcinogenic and mutagenic effects on the human body. With the increase in the release of VOCs, the environmental problems have become more and more severe. The haze, nitrogen oxides, sulfur dioxide, ammonia, and other toxic gases in the air will pose serious issue on human health and ecosystem. The monitoring and detection of toxic exhaust gases (such as nitrogen dioxide, ammonia, carbon monoxide and nitric oxide, etc.) play a crucial role in some areas such as environmental protection because they are highly toxic and may have adverse effects on ecosystems.

1.1 Hazardous toxic gases

Nitrogen dioxide (NO_2) is a toxic red-brown gas with a pungent odor and is an atmospheric pollutant with strong oxidizing properties. Due to the combustion of fossil fuels [1,2], the emission of nitrogen dioxide increases dramatically, which will cause acid rain and photochemical smog and will cause the destruction of ozone layer [3]. Additionally, the inhalation of nitrogen dioxide by the human body will damage the internal respiratory system and when its concentration exceeds up to 1 ppm, it will cause respiratory diseases and do harm to human organs and body [4]. Therefore, in order to avoid nitrogen dioxide pollution, it is necessary to developed real-time monitoring of this content in the environment with sensitive and selective sensor to detect the nitrogen dioxide. In the atmosphere, as shown in reaction (a) of Fig. 1, nitrogen dioxide can absorb light with a wavelength below 398 nm, resulting in photodissociation of nitrogen dioxide. This active oxidizing gas is the culprit for a series of nitrogen-containing pollutants such as nitrate per oxyacetylene (see Reaction b-g), and it eventually turns into acid rain. The hydrocarbons in the atmosphere will produce phenoxyacid groups, and PAN (reaction) is produced by the addition reaction with nitrogen dioxide. Exposed

to nitrogen dioxide in a long time can cause bronchiolitis, occlusive vasculitis, silo filler disease, and lung tissue inflammation. Plants that are exposed to ppm levels of nitrogen dioxide will interfere with chlorophyll synthesis and cause plant tissue breakdown. Exposed to higher concentrations of nitrogen dioxide will destroy plant photosynthesis. Nitrogen dioxide can also be used for the degradation of dyes and inks used in the textile industry. Nitrogen dioxide released by the aircraft in the atmosphere may damage the ozone layer in the stratosphere. Without the protection of the ozone layer, the Earth's surface organisms will be directly exposed to the ultraviolet radiation of the sun, leading to more severe environmental and health problems.

$$NO_2 + h\nu \ (<398\ nm) \rightarrow NO + O \qquad (a)$$
$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (b)$$
$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (c)$$
$$NO + NO_3 \rightarrow 2NO_2 \qquad (d)$$
$$O + NO_2 \rightarrow NO + O_2 \qquad (e)$$
$$NO_2 + NO_3 \rightarrow N_2O_5 \qquad (f)$$
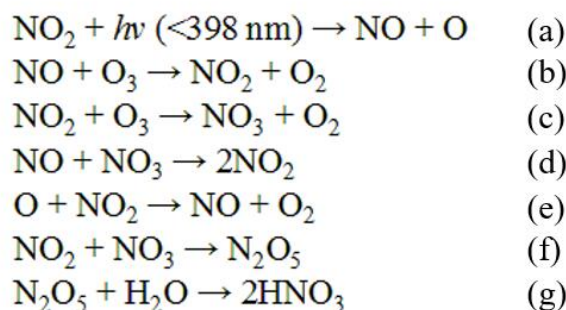$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad (g)$$

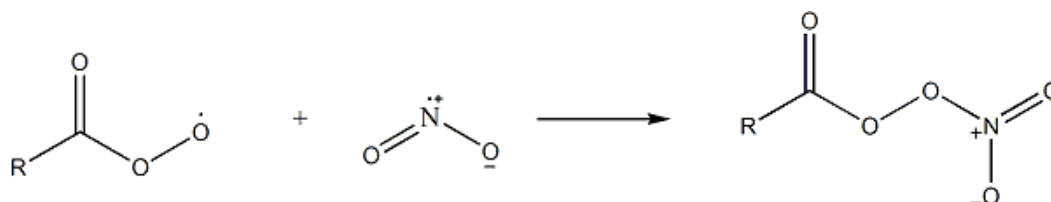Figure 1.1. The reaction between nitrogen oxides.

Figure 1.2. PAN Reaction

In addition to nitrogen oxides, ammonia gas is another harmful gas that is usually produced in the industry and is known for its corrosiveness and irritation. Inhalation of small amounts of ammonia can cause coughing, irritation of the nose and throat. Even at low concentrations of air or ammonia in the liquid, contact with the eyes or the skin can cause severe irritation. Exposure to concentrated ammonia solution for industrial use may even result in corrosive damage to the contact area, including permanent eye damage, skin burns, and even blindness [5]. Therefore, early detection and monitoring of ammonia on the job site may prevent workers and the environment from being

harmed.

Many developing countries are facing atmospheric pollution. This is mainly due to the imbalance in the rapid development of industrialization. It also leads to global warming and ecological imbalances. Therefore, the detection and monitoring of toxic gases such as nitrogen oxides and ammonia have attracted much attention due to their harmful effects on humans and the environment [6,7]. Therefore, the development of inexpensive, reliable, small-sized and low-power gas sensors with high performance is extremely important for environmental protection and industrial toxic gas monitoring [8,9].

1.2 The detection method of VOCs

Nowadays, there are many detecting methods for VOCs in the environment, such as spectrophotometry [10], chemiluminescence [11], chromatographic analysis [12] and other sensor.

For example, spectrophotometry is relatively economic, easy to carry and convenient operation, relatively mature sensing system, early application in the environmental monitoring department is more extensive, domestic research is also more, such as Hao W., etc. as early as in 1996 adopted UV derivative spectrophotometry concentration of benzene, toluene, and xylene in the air, the method does not require sample preparation, the procedure is fairly simple, it can be used for the determination of benzene, toluene, xylene and other substances in the air of the workshop, and is suitable for supervising and measuring the air quality of the workshop [13]. Spadavecchia et al. synthesized a series of metal phthalocyanine materials such as zinc, copper, and bismuth, and examined the IN-Vis absorption spectra of the interaction between films produced from above-mentioned materials and the VOCs vapors such as alcohols, esters, aldehydes, and ketones. The changes in the spectra were found to have a good response to VOCs [14]. Although this method is simple and practical, the operation is too cumbersome, which limits the wide application of the photometric method. Adam et al. conducted a research on detectors and achieved good results by replacing the thermal conductivity cell detector with a combination of GC-PSAD [15].

Most of these methods greatly limit their application due to high cost, complicated equipment, sophisticated operation steps, and long response time.

1.3 The classification of sensors

Due to the advantages of small size, portability, sensitivity and rapidity, and on-site detection, the sensor technology has been very popular in the analysis and detection of VOCs in recent years. The qualitative and quantitative detection of VOCs by sensor technology is very popular. The sensor can convert the concentration of the gas that cannot be directly measured into the acoustic signal, the optical signal, the electrical signal which can be directly measured. Gas sensor technology methods are mainly classified into the following categories: resistive semiconductor sensors, electrochemical sensors, solid electrolyte sensors, optical sensors, surface acoustic wave sensors, etc. [16]. Nowadays, many foreign research groups have introduced semiconductor nanotechnology into the VOCs sensors and achieved certain results. For example, Taurino et al. used the ultrasonic technology to prepare TiO_2 nanocrystalline films, and gas sensor arrays were made to identify various VOCs compounds [17]. Srivastava used a SnO_2 gas sensor array doped with Pd, Pt, and Au and an artificial neural network (ANN) to design a system for qualitative determination of methanol, acetone, methyl ethyl ketone, benzene, and xylene [18]. However, the current research in this area mainly remains at the laboratory stage, and the reported sensors that cannot be used in real environment. Therefore, the simple and rapid method for VOC detection in the atmosphere is still being continuously researched and developed. Although the sensor has the advantages of low cost, easy manufacturing, long life, low humidity sensitivity, and simple circuit, it also has many disadvantages such as low-level sensitivity, poor selectivity, limited life, poor repeatability, difficulty in miniaturization, and high power consumption [19].

As an alternative material, nanomaterial-based gas-sensing materials have gained widespread attention. Due to many excellent electrical, optical, and thermal properties as well as ultra-high specific surface area, they can respond and recover in a short time, with high sensitivity. Good selectivity, reversibility, and high stability [20]. Carbon

nanotubes (CNTs), graphene, graphene oxide (GO), reduced graphene oxide (rGO), fullerene, and carbon fiber (CF) [21-23], due to their remarkable physical and electrical properties, which are often used as chemical and biological sensors because they can be easily adjusted for sensitivity by simple chemical modification. For example, Wang et al. previously developed a high-impedance sensor based on single-walled carbon nanotubes (SWCNT). The sensor has an extremely fast response time, can recover in a short time and has good repeatability. It can be used to detect neurotoxins such as sarin agonists dimethyl methyl phosphonate (DMMP) [24]. They also produced sensors with a sensitivity of only 1 ppm to DMMP vapors, functionalized with cobalt phthalocyanine derivatives by π-π stacking to detect DMMP vapors [25].

1.4 The introduction of graphene

Graphene is a new type of material with two-dimensional structure. The hexagonal type formed by the ordered combination of sp^2 hybridized carbon atoms shows the honeycomb lattice plane. Graphene is a crystalline allotrope of carbon having two-dimensional properties. Its carbon atoms are densely packed in common atomic-scale hexagons. Each carbon atom has four bonds: one σ bond and each of three adjacent bonds and one outward facing π bond. The atomic distance is about 1.42 angstroms. The hexagonal lattice of graphene can be seen as two interlaced triangular lattices. This idea was successfully used to calculate the energy band structure of a single graphite layer using a tight-binding approximation [26].
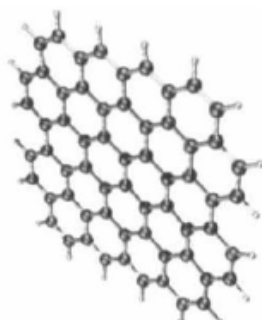

Figure 1.3. Graphene structure.[27]

The stability of graphene is due to its close-packed carbon atoms and sp^2 hybridization. The orbitals s, px and py constitute the σ bond, while the pz electrons form the π bond. After π-bond hybridization, π-bands and π-* bands are formed. These

half-filled energy bands allow electrons move freely, which is one of the reasons for the good electrical properties of graphene [26]. Solid form graphene sheets usually diffract on the (002) plane, and some single-walled nanostructures also have similar phenomena [28]. When graphene is exposed to carbon-containing molecules such as hydrocarbons, graphene can repair holes in its sheet itself. When bombarding graphene with pure carbon atoms, the atoms grow exactly as hexagons and fill all the pore sites [29]. Graphene is a two-dimensional plane consisting of ordered carbon atoms arranged in a honeycomb topology, with a thickness of only 1 carbon atom.
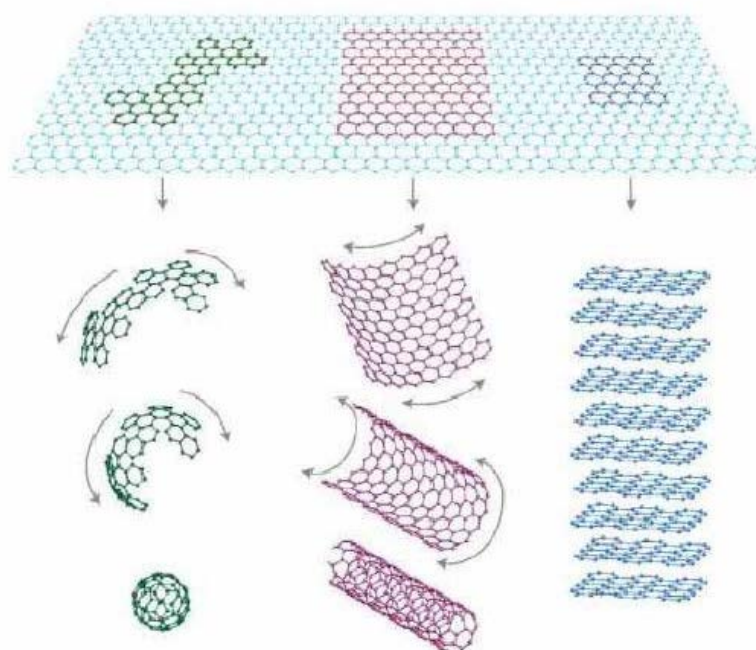

Figure 1.4. Graphene: the basic structural unit of carbon materials[27]

Due to its excellent optical, electrical, and mechanical properties, it has important application prospects in materials science, energy, biomedicine, and drug delivery. In terms of electrical properties, the carbon atoms of graphene are all sp^2 hybridized, and electrons with a p orbital constitute a π bond, and electrons can migrate freely, so graphene has excellent electrical properties. Carriers in graphene (Dirac fermions) can migrate at the speed of light and do not easily scatter, so graphene has extremely high charge mobility[30]. The single-layer graphene at room temperature has a very high mobility and a conductivity of about 10^6 S/m [31], which is the lowest resistivity material found at room temperature.

Graphene also has a great advantage in mechanics. In addition, because of its low density, it is a good reinforcing agent in the synthesis of composite materials, and it utilizes the interaction between its rich surface functional groups and other composite materials. Metals and other inorganic materials have advantages. In terms of thermal properties, allotropes of carbon have a high thermal conductivity, and the horizontal thermal conductivity of single-layer graphene in a suspended state is about 5×10^3 W/m·K [32]. The thermal conductivity of copper at room temperature is higher than that of copper.

Due to excellent electrical conductivity and thermal conductivity, graphene will be very promising in the field of microelectronic devices. Graphene can also block many gases, vapors, and liquids. Therefore, graphene can also be prepared into a number of composite materials that are resistant to corrosion and oxidation. Graphene has a large specific surface area, theoretically as high as 2600 m^2/g, which is much higher than that of carbon nanotubes (CNTs) reported so far (about 100 to 1000 m^2/g) [33]. Graphene can absorb visible light and infrared light, the absorption of visible light by single-layer graphene is only 2.3% [34]. Therefore, when the light intensity is increased, the irradiated graphene can easily become light saturated. Microsensors made of graphene can detect weaker gas signals, so graphene has great potential in the field of gas sensors. As a matter of fact, graphene is not an absolutely flat perfect surface, and a large number of defects exist in either the free-standing graphene or the graphene attached to the substrate.

Graphene has a benzene ring structure as a backbone, so it is chemically stable. Graphene can be modified by chemical methods. For example, the most commonly used Hummers method produces graphene oxide. After oxidation, many hydroxyl groups, carbonyl groups, carboxyl groups, and other oxygen-containing functional groups are inserted between graphene layers and improve the dispersibility in water.

However, the electrical conductivity of graphene after oxidation is greatly reduced, which has brought limitations to the development of conductance or electrochemical sensors. Fonseca et al. introduced conductive polymers (ie, PAni) into carbon fibers

(CF) [35]. PAni in PAni-CF composites is a highly conductive material. As the ratio of PAni to CF increases, the electrical conductivity of the composite increases. Therefore, the sensitivity and response speed of the gas sensor also increase. The experimental results show that the conductivity of PAni-CF composites changes dramatically with the adsorption of nitrogen dioxide gas. Although there is no quantitative recovery, but PAni-CF composites still can be used as NO_2 detector. These unique optical properties make graphene a widely used concern in the application of optical sensors.

1.5 Motivation of this work

In this dissertation, graphene oxide and polymers were used to prepare composite films for the detection of nitrogen dioxide gas. The main research area of graphene-based composites are graphene-carbon composites (fullerenes, carbon nanotubes), graphene-inorganic composites, and graphene-polymer composites, among which graphene-polymer composites It is a research hotspot. The commonly used methods for preparing graphene polymer composite materials include solution mixing, melt blending, and in-situ polymerization. Such composite materials can be processed into corresponding solutions by evaporation of solvents, solution coating, vacuum filtration, and layer self-assembly.

In this dissertation, numerous literature related to graphene and graphene oxide composites were mentioned, to understand the properties of graphene, preparation methods and characterization methods of graphene, and preparation techniques of graphene composite thin film materials. And proposing a novel design and synthesize procedure of graphene polymer composite film and apply it to detect various toxic gases at room temperature with improved the sensitivity and selectivity.

Chapter 2 Experimental Materials and Methods

2.1 Experimental materials and reagents

Name	Chemical formula	Purity	Production
Graphite	C	200 mesh	Alfa Aesar

Sulfuric acid	H_2SO_4	95-98%	Sinopharm chemical reagent
Potassium persulfate	$K_2S_2O_8$	99.99%	Sinopharm chemical reagent
Phosphorus pentoxide	P_2O_5	99%	Sinopharm chemical reagent
Potassium permanganate	$KMnO_4$	＞99.5%	Sinopharm chemical reagent
Hydrogen peroxide	H_2O_2	33%	Sinopharm chemical reagent
Hydrochloric acid	HCl	31%	Sinopharm chemical reagent
Poly (styrene sulfonic acid) sodium salt	PSS	M.W. 70000	Alfa Aesar
Silicon wafers	Silicon	P-doping	ZhejiangLijing Technology Co., Ltd.

2.2 Experimental equipment

Name	Type	Production
Electronic balance	ADVENTURER	OHAUS
Ultrasonic cleaner	KQ3200B type	Kunshan Ultrasonic Instrument Co., Ltd.
Ultrapure water equipment	UPT-II	Xian You Pu Co., Ltd.
Magnetic stirrer	DF-101S	Zhengzhou Ketai Co., Ltd.
High-speed centrifuge	Anke	Shanghai Anting Scientific Instrument Factory
Spin Coater	EZ4	Germany Schwan Co., Ltd
Fourier Transform Infrared Spectrometer (FRIT)	IRPrestige-21	Shimadzu Corporation
Atomic Force Microscopy (AFM)	Mutimode 8 Nanoscope V system	American Bruker Company
Transmission electron microscope (TEM)	JEM-2100	Japan Electronics Corporation (JEOL)
X-ray diffractometer (XRD)	D8-ADVANCE	Brooke AXS, Germany

UV spectrophotometer (UV)	Agilent8453	American Agilent Corporation

2.3 Preparation of materials

2.3.1 Preparation of GO and PSS solutions

(1) Synthetic graphene oxide (GO)

Graphene oxide was prepared using the Hummers' method [3]. Briefly, 4 mL H_2SO_4 (98%) with 0.85 g P_2O_5 and 0.85 g $K_2S_2O_8$ was used to pre-oxidized 0.5 g graphite powder. The pre-oxidized product was poured into a round bottom flask containing 20 mL of concentrated sulfuric acid, and 2.5 g of $KMnO_4$ was gradually added in ice bath. The reaction was kept at room temperature for 2 hours and then react for 2 hours at 35°C. Then 41.5 mL of deionized water was added dropwise and reacted for 2 hours. After that, 116.5 mL of deionized water and 3.3 mL of hydrogen peroxide solution were added, and the mixture was stirred for 2 hours to complete the reaction. Repeated centrifugation (8000 rpm, 10-15 min) and 4 washes with 1M concentrated hydrochloric acid. High-speed centrifugation (10000 rpm, 30 min), thoroughly washed with deionized water until the pH is about 6-7. The obtained graphene oxide was dispersed in water to prepare a 10 mg/mL solution.

（2）Sodium polystyrene sulfonate (PSS) solution

Weigh 0.5 g of sodium polystyrene sulfonate solids, add 100 mL of deionized water, stir until dissolved, and obtain a 5 mg/mL PSS solution.

2.3.2 Hydrophilic treatment of silicon wafers

The Piranha solution was prepared. Mixing concentrated sulfuric acid with hydrogen peroxide in a volumetric ratio of 7:3 removes the organic residue from the surface of the silicon wafer. It is a strong oxidizing agent that removes most of the organic material and introduce hydroxyl groups on the surface. The silicon wafer was immersed in a piranha solution and placed in an oven at a temperature of 105°C for 1.5 hours. The treated silicon wafer was highly hydrophilic and was easily covered with graphene oxide and polymer.

2.3.3 Preparation of Composite Films

In this experiment, a PSS+GO composite film was prepared using a spin coater.

The sizing process for preparing the composite film by spin coating is divided into three steps: dispensing, high-speed rotation, and drying (solvent evaporation). First, the solution was dropped on the center of the substrate (silicon wafer), and the speed of the spin coater was adjusted to 1600 r/min for a duration of 20 sec. The silicon wafer will be coved full with solution on the surface. The solution will move toward the edge of the substrate under the influence of centrifugal force, and the film will gradually become thin and uniform.

Chapter 3 Results and Discussion

From the experimental sample, it can be concluded that when the thickness of the film is different, the color of the film will also change, which is due to the principle of thin film interference. Thin film interference is a natural phenomenon. The most common examples are colored oil layers in water, or soap bubbles colored in sunlight. This is due to the fact that when the light is incident, light waves reflected by the upper and lower edges of the film interfere with each other, enhancing or reduce reflected light. The thickness of the film can be nanometer or micrometer range.
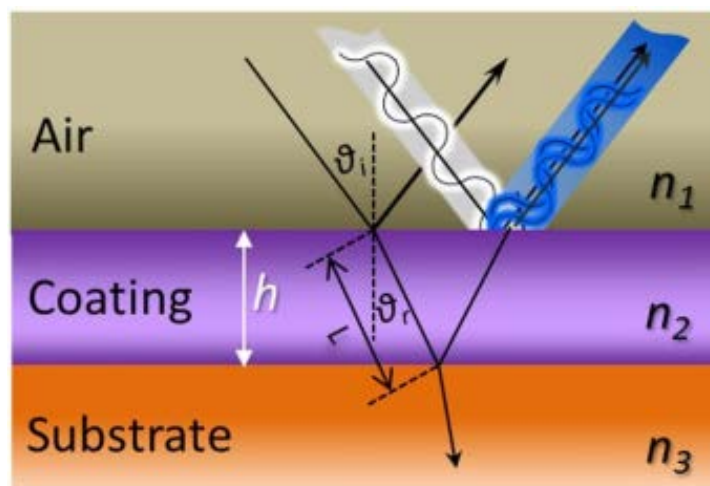

Figure 2.1. Light incident on a coating substrate.[36]

After expansion, the thickness of the membrane is changed to reflect visible light with different wavelengths. The mechanism is shown in the figure below.
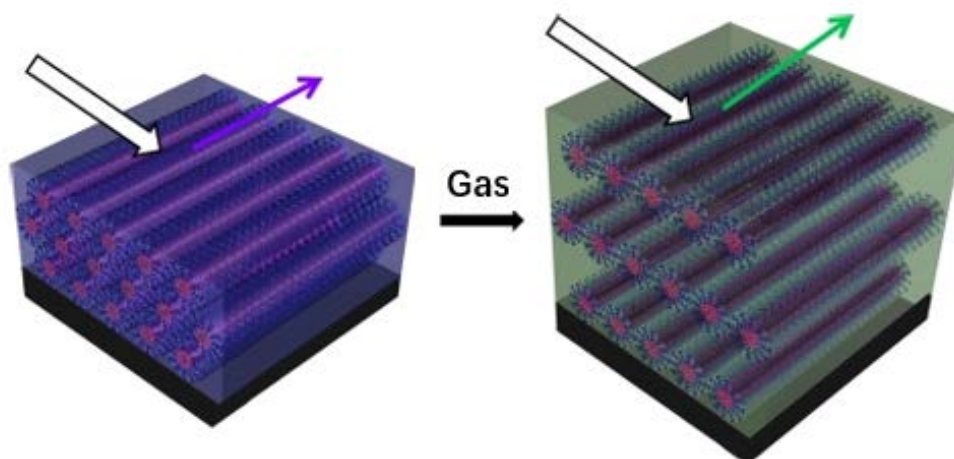
Figure 2.2. The mechanism the changes of thickness.[37]

The films prepared on the hydrophilic treated silicon wafers were spin-coated with different concentrations of GO, and the diameter of the silicon wafers was 25.4±0.3 mm, shown in Figure 3.1. Try to spin-coat the GO and PSS solutions, GO and PVA solutions, respectively, using a layered coating method to obtain the samples shown in Figure 3.2.
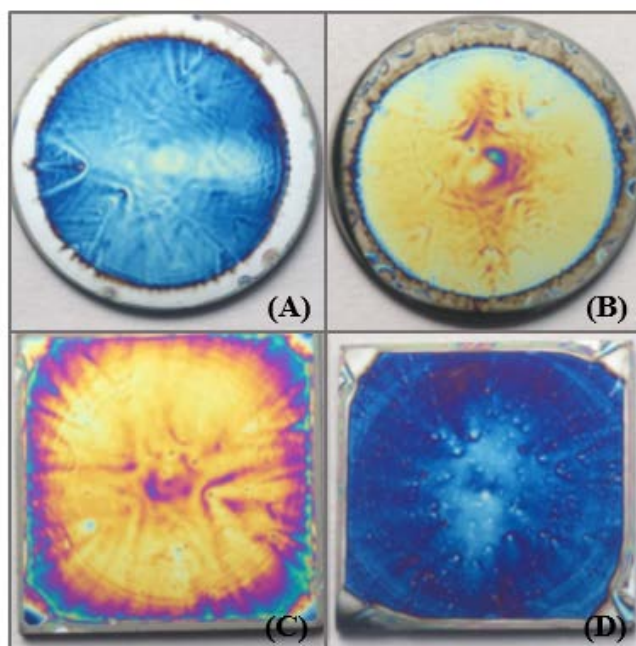

Figure 3. (A) (GO/GO)7 GO:5mg/mL (B) (GO/GO)10 GO:5mg/mL

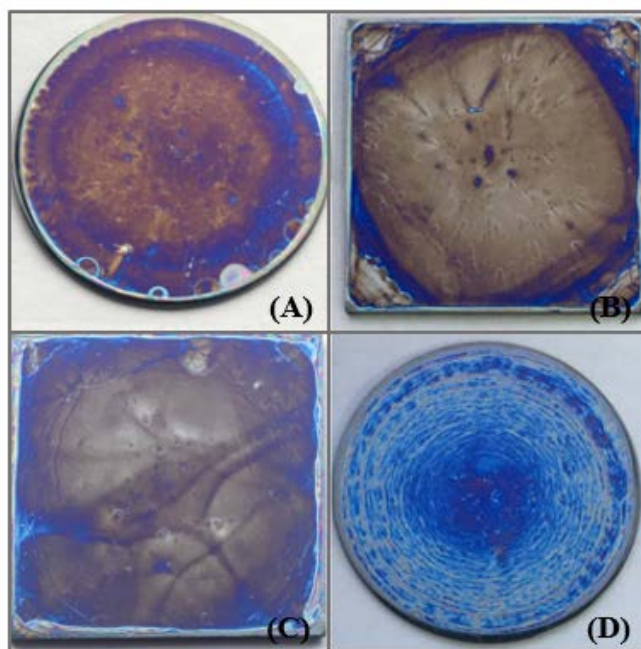(C) (GO/GO)10 GO:3mg/mL (D) (GO/GO)7 GO:6mg/mL

Figure 4. GO：3mg/mL PSS：5mg/mL (A) (GO/PSS)10 (B) (PSS/GO)10

GO：1mg/mL PVA：6.7mg/mL (C) (GO/PVA)7 (D) (PVA/GO)7

Comparing Figure 3. (A) (B), it can be seen that when the solution concentration is the fixed, the thicker the film, the color of the film will shift from blue to yellow. Comparing Figure 3. (B) (D), when the number of spin coats is the same, the higher the solution concentration, the larger the film thickness, and the color also shifts to yellow. As there is no clean-room, Figure 3. (D) shows that there are many obvious small particles on the surface, affecting the overall effect of the film, the experimental environment needs to be improved. Figure 3. (C) shows that the solution concentration is too high, and the film thickness is more uneven. In physics, the "coffee ring" effect refers to the trace left by the evaporation of the liquid containing the particles. The liquid evaporated from the edge during the evaporation process is supplemented by the internal liquid [38], which results that the edge will be thicker.

In Figure 4., all the films were produced in a layer by layer coating manner. Figure 4. (C) (D) is a laminate of PVA and GO layers. Since the groups between PVA and GO are hydrophobic, they cannot be perfectly bonded to silicon. In a layer-by-layer coating, the films made of PSS and GO in Figure. 4. (A) (B) are also very non-uniform.

Based on this, a mixed spin-coating method is conducted, in which to mix

graphene oxide solution (10 mg/mL) with sodium polystyrene sulfonate solution (5 mg/mL) in a volume of 2:1. Spin-coated on a silicon wafer that has been hydrophilically treated, the sample as figure 5. was obtained. A uniform sample was cut from a large silicon wafer having a diameter of 10 cm that had been spin coated.
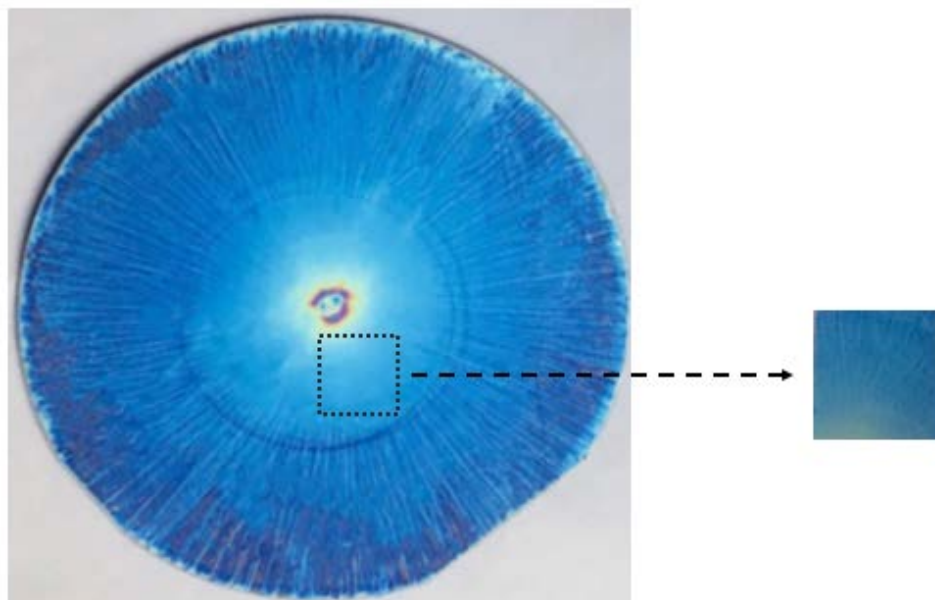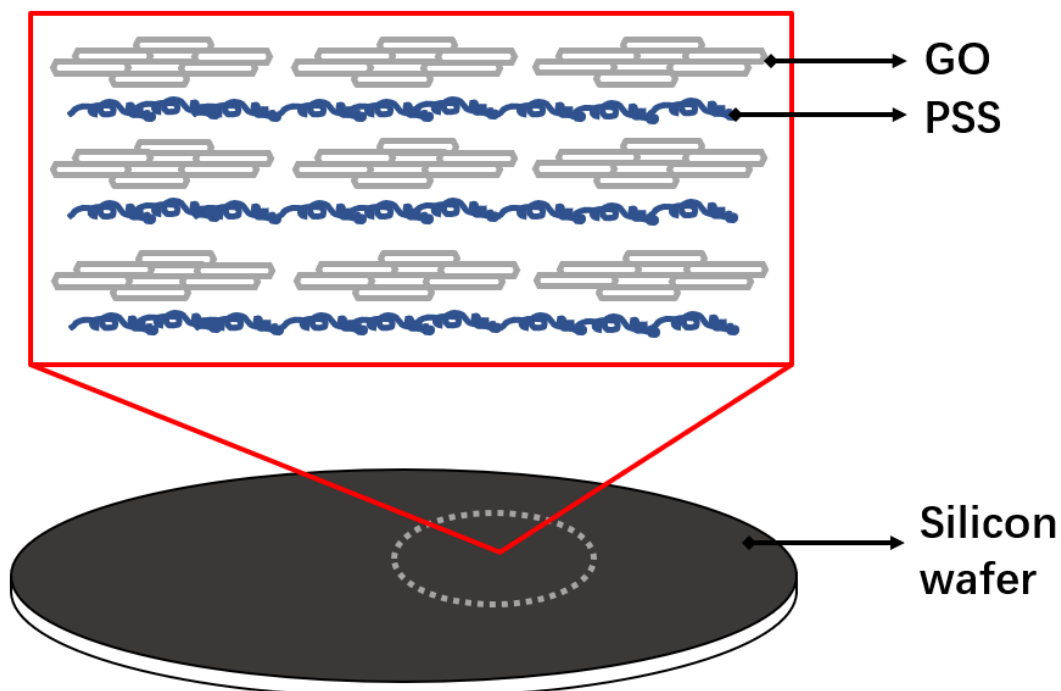

Figure 5. The film of PSS+GO.

Figure 6. Scheme of the film of PSS+GO.

Figure 6. is a schematic of a PSS/GO composite thin film. When gases pass through the film, it will temporarily stay in the PSS and GO layers between the films, affecting the thickness of the film and causing the film color to change.

3.1 Fourier Transform Infrared Spectrometer (FRIT) of GO

After the oxidation treatment, the graphene oxide still maintains the layered structure of the graphene, but many oxo functional groups are introduced on the surface of graphene. Fourier transform infrared spectroscopy (FTIR) was used to analyze the functional groups of GO. Figure 7. (A) shows the infrared spectrum of graphite and Figure 7. (B) shows the GO infrared spectrum. As shown in the figure, the peaks appearing near (3418 cm^{-1}) in Figure 7. (B) represent the stretching vibration peaks of -OH groups, which are still at 1062 cm^{-1}, 1224 cm^{-1}, and 1388 cm^{-1}. Absorption peaks appeared at 1622 cm^{-1} and 1710 cm^{-1}, which represent the stretching vibrations of C-O, C-O-C, C-OH, C=C and C=O groups, respectively. The presence of these oxygen-containing groups indicates that the graphite has been fully oxidized during the experiment. The surface of the synthesized GO is rich in functional groups such as hydroxyl and carboxyl groups. In particular, the presence of hydroxyl groups makes graphene oxide extremely easy to form hydrogen bonds with water molecules and thus readily soluble in water.
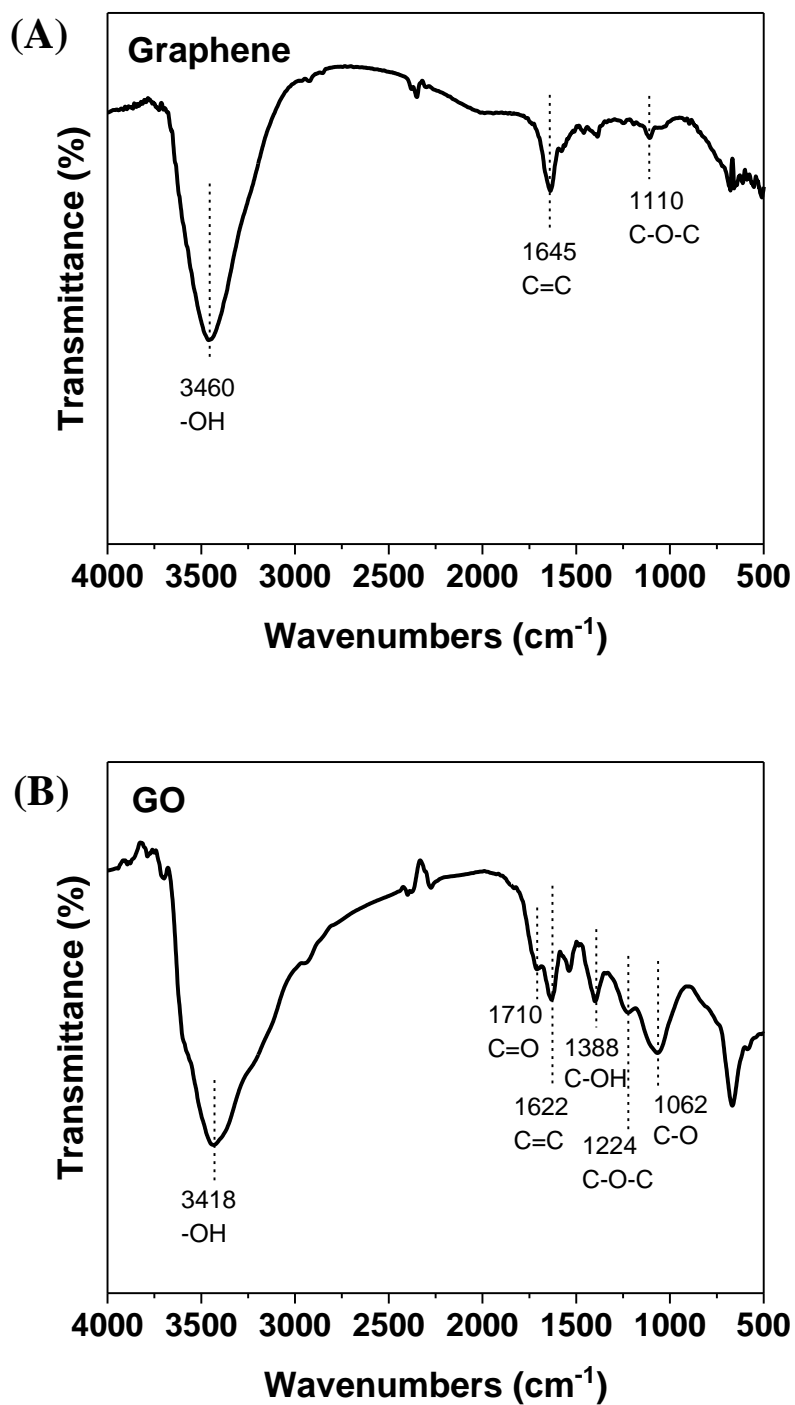
(A) Graphene

Transmittance (%)

Wavenumbers (cm⁻¹)

3460
-OH

1645
C=C

1110
C-O-C

(B) GO

Transmittance (%)

Wavenumbers (cm⁻¹)

3418
-OH

1710
C=O

1622
C=C

1388
C-OH

1224
C-O-C

1062
C-O

Figure 7. (A) FTIR of Graphite; (B) FTIR of GO.

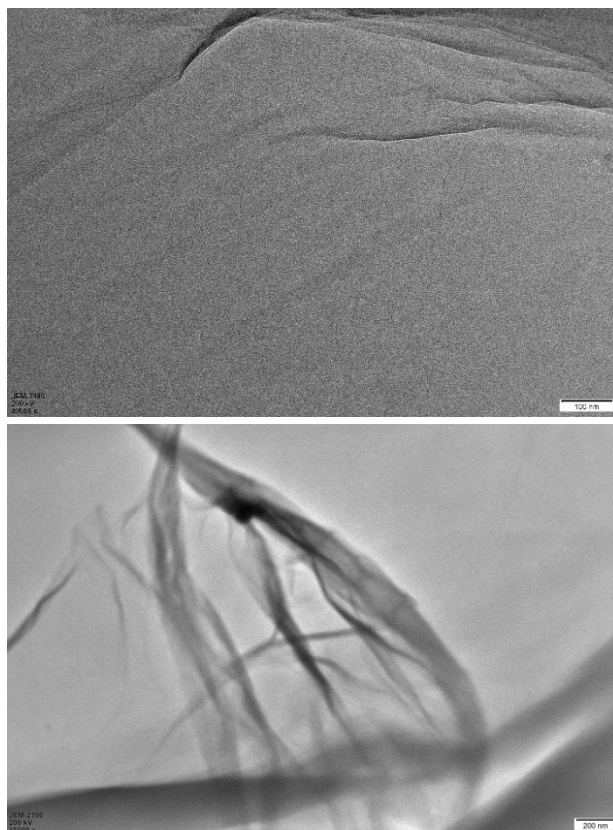## 3.2 Transmission electron microscope (TEM) of the films

Figure 8. TEM images of (PSS/GO)

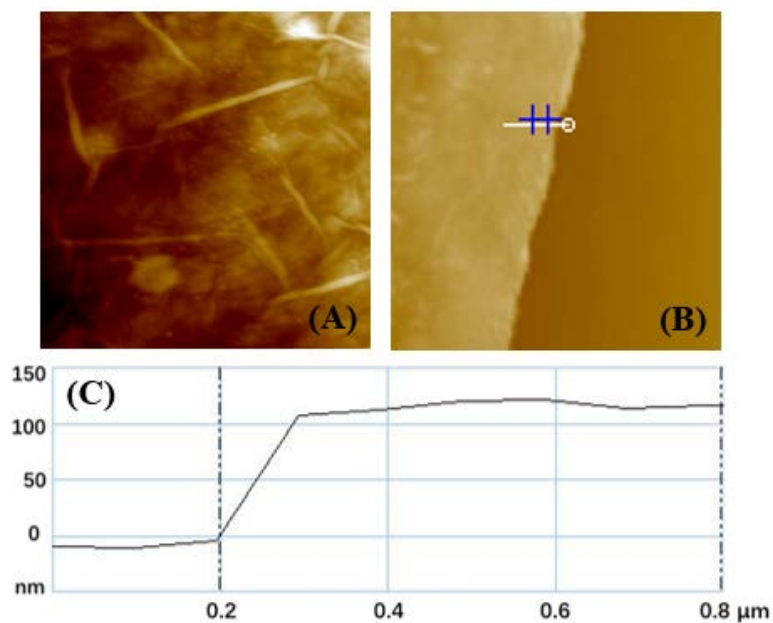## 3.3 Atomic Force Microscopy (AFM) of the films

Figure 9. (A) The AFM images of the surface of PSS/GO film. (B) The AFM images of the cross-section of PSS/GO film. (C) The analysis of the thickness of PSS/GO film.

Figure 9. (A) is a surface view of the composite thin film under an atomic force microscope. The AFM shows that the film attached to the silicon wafer has some wrinkles due to the wrinkled structure of the graphene itself. (B) is a uniform cross-sectional image of a PSS+GO film with a thickness about 125±5 nm attached to a Si wafer. The thickness of the film can be controlled by adjusting the concentration of the GO aqueous suspension and the rotational speed of spin coating and number of layers.
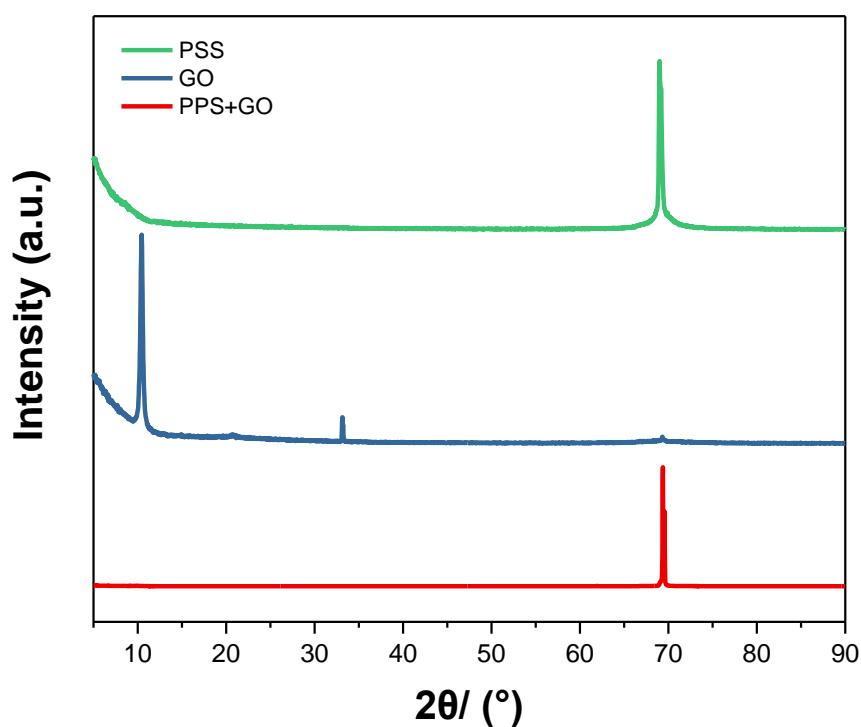
3.4 X-ray diffractometer (XRD) of the films

Figure 10. XRD spectrum of PSS film, GO film and (PSS+GO) film.

Figure 10 shows XRD patterns of PSS film, GO film and PSS-GO film. It is found that PSS and PSS-GO film has characteristic diffraction peaks around $2\theta=70°$ and GO is about $2\theta=10°$ peak.

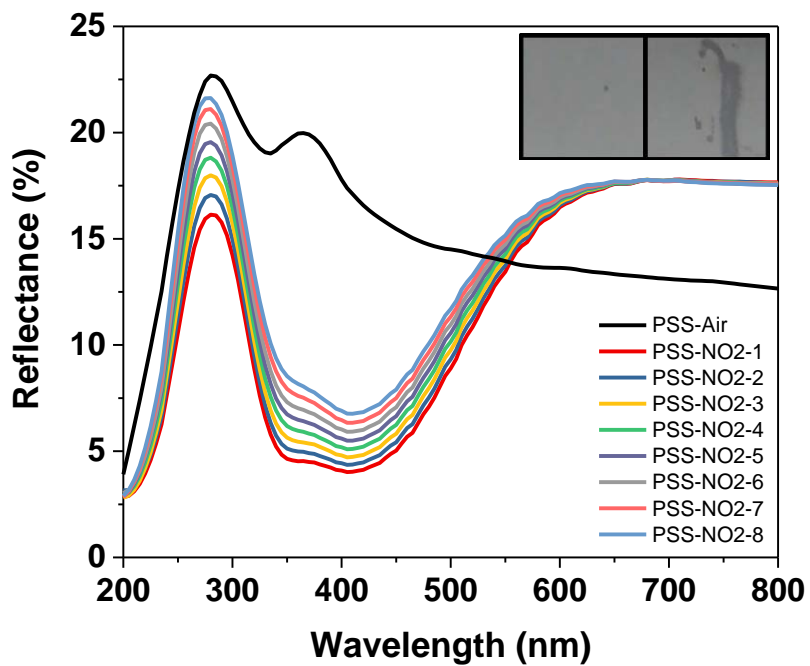## 3.5 The response to nitrogen dioxide of the composite film

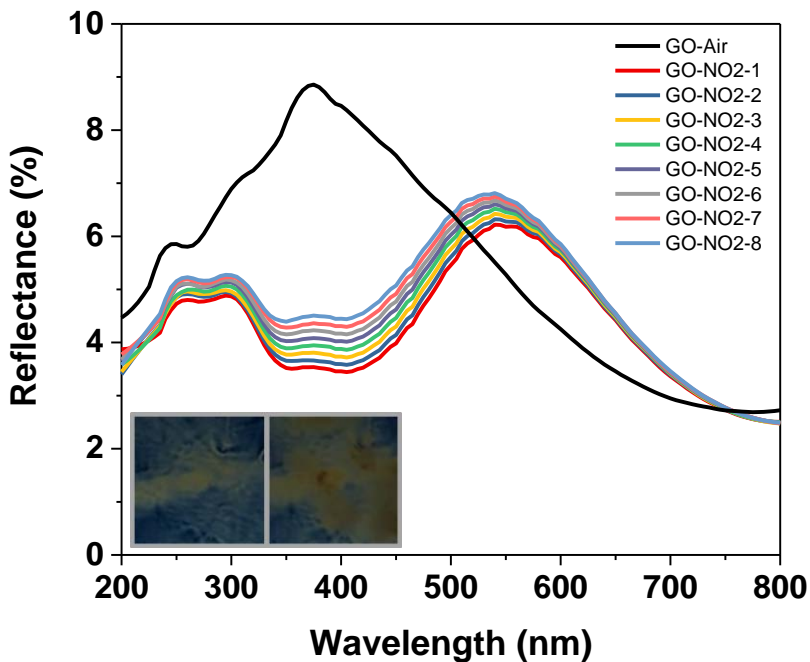Figure 11. The reflectance of PSS film in NO_2 atmosphere.

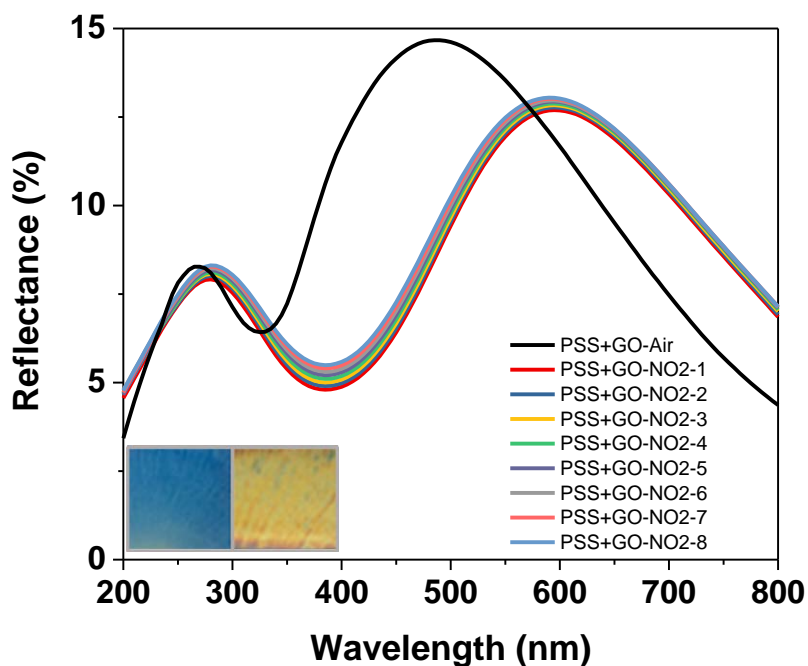Figure 12. The reflectance of GO film in NO_2 atmosphere.

Figure 13. The reflectance of PSS+GO film in NO_2 atmosphere.

Comparing the pure PSS film, GO film and PSS/GO composite film, it was finally determined that the composite film was the most sensitive to nitrogen dioxide response, and the composite thin-layer color changed from blue to yellow in the nitrogen dioxide atmosphere and can restore the original in a short time. Placing the PSS/GO composite film in a carbon dioxide atmosphere, the composite film will respond significantly and the color will change from blue to yellow.
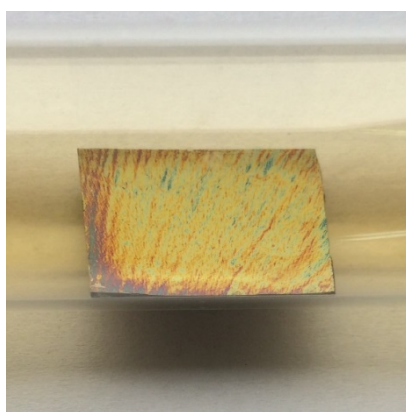

Figure 14. PSS+GO film in the NO_2 atmosphere.

3.6 The selectivity of PSS/GO composite film

In addition to response to nitrogen dioxide gas, PSS/GO composite films were also

tested for other gases, such as ammonia, ethanol vapor, etc., and characterized by UV.
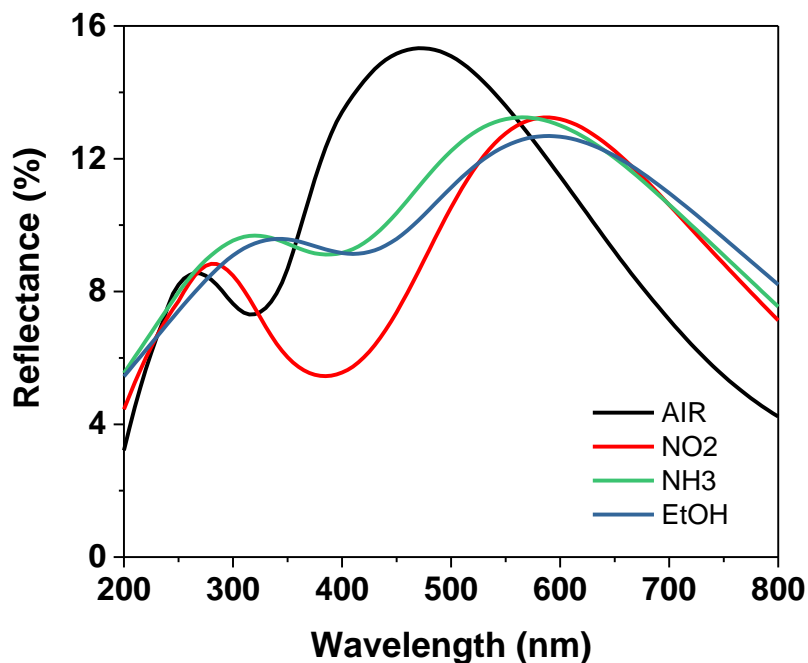

Figure 15. PSS/GO film in different atmosphere.

The PSS/GO composite film was also test for others nine organic pollutants, UV spectrum shows that there is almost no response to those gases, it means the film has good selectivity.

Name	Hexane	Toluene	CH_2Cl_2	$CHCl_3$	Ethyl ether	Ethyl acetate	THF	Acetonitrile	DMSO
Molecular weight	86.18	92.14	84.93	119.4	74.1	88.1	72.1	41.05	78.13
Polarity	0.0	2.4	3.1	4.1	4.2	4.4	5.0	5.8	7.2
Boiling point	69	110.6	39.75	61.3	34.6	77	66	81.6	189
Hydroph-ilicity	×	×	×	×	√	√	√	√	√

Chapter 4 Conclusions

In this thesis, numerous literature related to graphene and graphene oxide composites are reviewed, and the properties of graphene, preparation methods and

characterization methods of graphene, and preparation techniques of graphene-based composite thin film materials are thoroughly studied. It also proposed to design and synthesize graphene/PSS materials and apply them to the detection of various toxic gases at room temperature in order to improve the sensitivity characteristics (sensitivity, selectivity) of gas sensors. The materials prepared in this paper were subjected to detailed morphology and structure characterization and a series of gas sensitivity tests. The main conclusions are as follows:

(1) Infrared (FTIR) and testing were performed on the graphene oxide prepared to explore a method for quickly and accurately characterizing graphene oxide.

(2) PSS/GO composite film was prepared by spin coating. Transmission electron microscopy (TEM), atomic force microscopy (AFM) and X-ray diffraction (XRD) were used to characterize the morphology and composition of the films.

(3) Detect the gas sensitivity of composite films to various gases. The composite film has the most sensitive response to nitrogen dioxide, and also can responds to other gases like ethanol vapor, ammonia.

References

[1] W. Gopel, T. A. Jones, M. Kleitz, I. Lundstrom, and T. Seiyama, "Sensors, A Comprehensive Survey, Volume 3, Part II, Chemical and Biochemical Sensors," 2008.

[2] N. A. Luechinger, E. K. Athanassiou, and W. J. Stark, "Graphene-stabilized copper nanoparticles as an air-stable substitute for silver and gold in low-cost ink-jet printable electronics," *Nanotechnology,* vol. 19, no. 44, p. 445201, 2008.

[3] J. D. Fuentes and M. Demetsky, "CARBON MONOXIDE PRODUCTION IN RESPONSE TO INCREASED REFORESTATION AND TRAFFIC IN EASTERN UNITED STATES," *Field Studies,* 2003.

[4] P. L. Wang and H. H. Shen, "[Outdoor air pollution and asthma]," *Zhonghua Jie He He Hu XI Za Zhi,* vol. 26, no. 2, pp. 109-111, 2003.

[5] S. Gupta Chatterjee, S. Chatterjee, A. K. Ray, and A. K. Chakraborty, "Graphene–metal oxide nanohybrids for toxic gas sensor: A review," *Sensors and Actuators B: Chemical,* vol. 221, pp. 1170-1181, 2015.

[6] R. Atkinson, "Atmospheric chemistry of VOCs and NOx," *Atmospheric Environment,* vol. 34, no. 12, pp. 2063-2101, 2000/01/01/ 2000.

[7] D. Zhang *et al.*, "Detection of NO2 down to ppb Levels Using Individual and Multiple In2O3 Nanowire Devices," *Nano Letters,* vol. 4, no. 10, pp. 1919-1924, 2004/10/01 2004.

[8] Q. M. Konopacky, T. S. Barman, B. A. Macintosh, and C. Marois, "Detection of Carbon Monoxide and Water Absorption Lines in an Exoplanet Atmosphere," *Science,* 10.1126/science.1232003 vol. 339, no. 6126, p. 1398, 2013.

[9] J. Yu, D. Zhao, X. Xu, X. Wang, and N. Zhang, "Study on RuO2/SnO2: Novel and Active Catalysts for CO and CH4 Oxidation," *ChemCatChem,* vol. 4, no. 8, pp. 1122-1132, 2012/08/01 2012.

[10] A. Aydın, O. Ercan, Zgen, and S. Taşcıoğlu, "A novel method for the spectrophotometric determination of nitrite in water," *Talanta,* vol. 66, no. 5, p. 1181, 2005.

[11] Y. Kanda and M. Taira, "Chemiluminescent method for continuous monitoring of nitrous acid in ambient air," *Analytical Chemistry,* vol. 62, no. 19, p. 2084, 1990.

[12] Y. Q. Li, K. L. Demerjian, M. S. Zahniser, D. D. Nelson, J. B. Mcmanus, and S. C. Herndon, "Measurement of formaldehyde, nitrogen dioxide, and sulfur dioxide at Whiteface Mountain using a dual tunable diode laser system," *Journal of Geophysical Research Atmospheres,* vol. 109, no. D16, pp. -, 2004.

[13] S. Nakamura and S. Daishima, "Simultaneous determination of 22 volatile organic compounds, methyl- tert -butyl ether, 1,4-dioxane, 2-methylisoborneol and geosmin in water by headspace solid phase microextraction-gas chromatography–mass spectrometry," *Analytica Chimica Acta,* vol. 548, no. 1, pp. 79-85, 2005.

[14] O. A. Attanasi, G. Ciccarella, P. Filippone, G. Mele, J. Spadavecchia, and G.

Vasapollo, "Novel phthalocyanines containing cardanol derivatives," *Journal of Porphyrins & Phthalocyanines,* vol. 7, no. 01, pp. -, 2003.

[15]   A. K. Wanekaya, M. Uematsu, M. Breimer, and O. A. Sadik, "Multicomponent analysis of alcohol vapors using integrated gas chromatography with sensor arrays," *Sensors & Actuators B Chemical,* vol. 110, no. 1, pp. 41-48, 2005.

[16]   A. M. Andringa, C. Piliego, I. Katsouras, P. W. M. Blom, and D. M. D. Leeuw, "NO2 Detection and Real-Time Sensing with Field-Effect Transistors," *Chemistry of Materials,* vol. 26, no. 1, pp. 773-785, 2014.

[17]   A. M. Taurino *et al.*, "Nanostructured TiO2 thin films prepared by supersonic beams and their application in a sensor array for the discrimination of VOC," *Sensors and Actuators B: Chemical,* vol. 92, no. 3, pp. 292-302, 2003/07/15/ 2003.

[18]   A. K. Srivastava, "Detection of volatile organic compounds (VOCs) using SnO2 gas-sensor array and artificial neural network," *Sensors and Actuators B: Chemical,* vol. 96, no. 1, pp. 24-37, 2003/11/15/ 2003.

[19]   X. Liu, S. Cheng, H. Liu, S. Hu, D. Zhang, and H. Ning, "A Survey on Gas Sensing Technology," *Sensors,* vol. 12, no. 7, 2012.

[20]   G. Jimenez-Cadena, J. Riu, and F. X. Rius, "Gas sensors based on nanostructured materials," *Analyst,* 10.1039/B704562J vol. 132, no. 11, pp. 1083-1099, 2007.

[21]   J. Huang and Q. Wan, "Gas Sensors Based on Semiconducting Metal Oxide One-Dimensional Nanostructures," *Sensors,* vol. 9, no. 12, 2009.

[22]   S. S. Varghese, H. S. Varghese, S. Swaminathan, K. K. Singh, and V. Mittal, "Two-Dimensional Materials for Sensing: Graphene and Beyond," *Electronics,* vol. 4, no. 3, 2015.

[23]   W. Zhao, C. Yang, D. Zou, Z. Sun, and G. Ji, "Possibility of gas sensor based on C20 molecular devices," *Physics Letters A,* vol. 381, no. 21, pp. 1825-1830, 2017/06/09/ 2017.

[24]   W. Yanyan, Z. Zhihua, Y. Zhi, C. Xiaohang, X. Dong, and Z. Yafei, "Gas sensors based on deposited single-walled carbon nanotube networks for DMMP detection," *Nanotechnology,* vol. 20, no. 34, p. 345502, 2009.

[25]   Y. Wang *et al.*, "Flexible gas sensors with assembled carbon nanotube thin films for DMMP vapor detection," *Sensors and Actuators B: Chemical,* vol. 150, no. 2, pp. 708-714, 2010/10/28/ 2010.

[26]   D. R. Cooper *et al.*, "Experimental Review of Graphene," *ISRN Condensed Matter Physics,* vol. 2012, pp. 1-56, 2012.

[27]   A. K. Geim and K. S. Novoselov, "The rise of graphene," *Nature Materials,* vol. 6, p. 183, 03/01/online 2007.

[28]   D. Kasuya, M. Yudasaka, K. Takahashi, F. Kokai, and S. Iijima, "Selective Production of Single-Wall Carbon Nanohorn Aggregates and Their Formation Mechanism," *The Journal of Physical Chemistry B,* vol. 106, no. 19, pp. 4947-4951, 2002/05/01 2002.

[29]   R. Zan, Q. M. Ramasse, U. Bangert, and K. S. Novoselov, "Graphene Reknits Its Holes," *Nano Letters,* vol. 12, no. 8, pp. 3936-3940, 2012/08/08 2012.

[30] P. Ramesh, S. Bhagyalakshmi, and S. Sampath, "Preparation and physicochemical and electrochemical characterization of exfoliated graphite oxide," *Journal of Colloid & Interface Science,* vol. 274, no. 1, pp. 95-102, 2004.

[31] K. I. Bolotin *et al.*, "Ultrahigh electron mobility in suspended graphene," *Solid State Communications,* vol. 146, no. 9, pp. 351-355, 2008.

[32] F. Schedin *et al.*, "Detection of individual gas molecules adsorbed on graphene," *Nature Materials,* vol. 6, no. 9, pp. 652-655, 2007.

[33] R. Das, M. E. Ali, S. B. A. Hamid, S. Ramakrishna, and Z. Z. Chowdhury, "Carbon nanotube membranes for water purification: A bright future in water desalination," *Desalination,* vol. 336, pp. 97-109, 2014/03/03/ 2014.

[34] N. RR *et al.*, "Fine Structure Constant Defines Visual Transparency of Graphene," *Science,* vol. 320, no. 5881, pp. 1308-1308, 2008.

[35] C. P. Fonseca, D. A. L. Almeida, M. R. Baldan, and N. G. Ferreira, "NO2 gas sensing using a CF/Pani composite as electrode," *Ecs Transactions,* vol. 41, no. 21, pp. 21-28, 2012.

[36] L. Yu *et al.*, "Ultrafast colorimetric humidity-sensitive polyelectrolyte coating for touchless control," *Materials Horizons,* vol. 4, no. 1, 2016.

[37] E. Kim, S. Y. Kim, G. Jo, S. Kim, and M. J. Park, "Colorimetric and resistive polymer electrolyte thin films for real-time humidity sensors," *ACS Appl Mater Interfaces,* vol. 4, no. 10, pp. 5179-87, Oct 24 2012.

[38] R. D. Deegan, O. Bakajin, and T. F. Dupont, "Capillary flow as the cause of ring stains from dried liquids," *Nature,* vol. 389, no. 6653, pp. 827-829, 1997.

Acknowledgments

Foremost, I would like to express my sincere gratitude to my advisor Prof. Hong Chi for the continuous support of my thesis, for her patience, motivation, enthusiasm, and immense knowledge. Her guidance helped me in all the time of experiment and writing of this thesis. I could not have imagined having a better advisor and mentor for my thesis. Besides my advisor, I would also like to thank senior apprentices Gong Tingyuan, Zhang Xiaoxiao, Song Xiuhuan whose very supportive. Last but not the least, I would like to thank my family for giving birth to me in the first place and supporting me spiritually throughout my life.