Preparation of Fluorescent GOs and Its Application in Heavy Metal Ions Detection

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Contents

Abstract

Tea contains catechins, cholestones, caffeine, inositol, folic acid, pantothenic acid and other ingredients, can improve human health. Therefore, the tea is loved by the "one of the world's three drinks" reputation. But now, some unscrupulous traders in the tea by adding copper ions, want to change the old tea tea. Copper ion is one of the essential trace elements in the human body, but when it is too high, it will bring a lot of damage to the human body. Therefore, we want to use fluorescent oxide graphene to detect copper ions, because copper ions have fluorescence quenching properties. And many heavy metals have similar properties, if the fluorescent oxide graphene can detect copper ions, it must be able to detect many other heavy metal ions.

To graphite as raw material, after several oxidation, the final product of fluorescent oxide graphene. In the first pre-oxidation, the first 8000-purpose graphene and potassium persulfate and phosphorus pentoxide in concentrated sulfuric acid catalyzed reaction, the pre-oxidation products. And then pre-oxidation products through concentrated sulfuric acid and potassium permanganate oxidation of the first oxidation products. The first oxidation product was treated with Piranha solution, and the resulting second oxidation product was fluorinated graphene. The resulting fluorescent oxide graphene in the face of copper ions and other heavy metal ions, will make it fluorescence quenching, so as to achieve the purpose of detection.

Keywords: fluorescence; oxidized graphene; copper ions

Chapter 1   Introduction

1.1 Introduction of graphene

1.1.1 Properties of graphene

Since 2004, the University of Manchester scientists Geim and Novoselov mechanical cutting method from the graphite separation of graphene, graphene because of its unique physical and chemical properties caused widespread concern. Graphene is a novel two-dimensional atomic crystal composed of a single atom layer composed of carbon atoms connected by sp^2. The basic structural unit is a stable benzene six-membered ring.[1] Graphene ten minutes graphite form of carbon nanomaterials of the matrix, it can be wrapped into a spherical shape to get zero-dimensional fullerenes, crimped into a tube to get one-dimensional carbon nanotubes, the accumulation of three-dimensional graphite.[2]

The charm of graphene lies not only in its magical two-dimensional structure, but also in its unique physical and chemical properties. Graphite has a large surface area, the theoretical reported in the literature is 2630 m^2/g.[3] Graphene has good mechanical properties, its Young model and the intrinsic strength of 1 Tpa and 130 Gpa, respectively, is more than 100 times the steel, is currently the highest known material.[4] Graphene good thermal conductivity, the thermal conductivity of 5000 $Wm^{-1}K^{-1}$, is three times the diamond. The graphene also exhibits excellent field-effect semiconductor properties with carrier mobility of up to 15000 $cm^2V^{-1}s^{-1}$, which is currently known to be twice as high as that of the indium antimonide material with the highest mobility more than 10 times the mobility of commercial silicon. In certain circumstances (such as low temperature quenching, etc.), its mobility can even reach 250,000 $cm^2V^{-1}s^{-1}$. In addition, graphene also has a perfect quantum Hall effect,

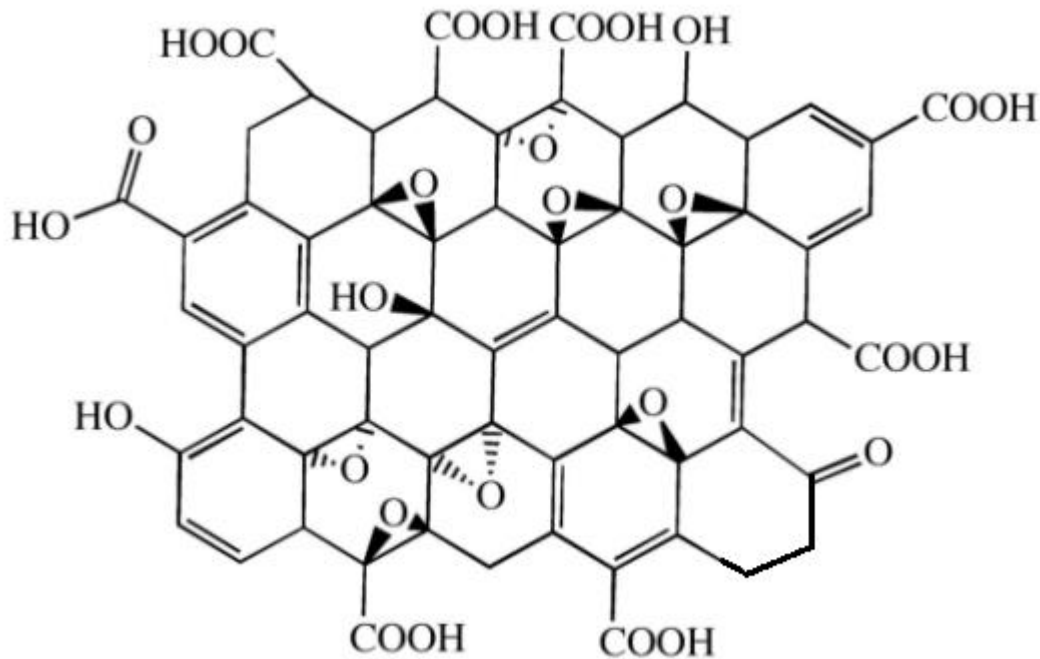ferromagnetism and giant magnetoresistance effect.[5-6]

Figure 1-1: Structure of Oxidized Graphene

1.1.2 Preparation of graphene

At present, the methods of preparing graphene has two different types: Physical methods and chemical methods. Physical method is that using high lattice and Complete cheap graphite or graphite as raw materials, prepare monolayer or multilayer graphene through micro-mechanical peeling method, thermal expansion peeling method and so on. This method is easy to obtain raw materials, synthetic graphene higher purity, less defects, but time-consuming, is not conducive to large-scale production. At present, laboratory graphene is mainly prepared by chemical method, which is mainly through the synthesis of small molecules or solution separation method to synthesize graphene.

（1）Micromachined.

The micromachined stripping method was first used as a physical method for the

preparation of graphene. □As early as 1999, Lu et al. etched the graphite layer with a thickness of 200 nm on the pyrolytic graphite oriented at a height of the SiO_2 substrate with oxygen plasma etching. In 2004, the University of Manchester, Geim and so on for the first time with a tape from the graphite layer on the layer of the preparation of a single layer of graphene. Geim et al. Etched some microchannels on the highly oriented pyrolytic graphite using an ion beam, then glued to the glass substrate with a photoresist, and then repeatedly torn with a clear tape to remove excess pyrolytic graphite After the microcapsules of the glass substrate into the acetone solvent ultrasonic, and then the monocrystalline silicon into the handle in the whole body, you can single layer of graphene 'fish out'. Micro-mechanical cutting can provide high-quality graphene for basic physical research, but the problem is that it is difficult to obtain large quantities of graphene.

（2）Thermal expansion peeling or solvent peeling

The monolayer or multi-layer graphene is usually prepared by directly stripping or removing graphite from polystyrene or expanded graphite by heating, or by adding it to a solvent and then stripping with ultrasonic waves. Schniepp et al. placed the graphite oxide in a closed quartz tube and heated to 1050 ° C for 30 seconds under nitrogen protection conditions to obtain graphene. At high temperatures, the oxygen-containing functional groups on the graphene oxide decompose to produce CO_2 and CO_2 into the gaps of the lamellae, allowing the layers to be peeled off to produce graphene. Coleman et al. refers to the method of stripping carbon nanotubes by liquid phase to disperse the graphite first in N-methyl-pyrrolidone and to obtain graphene by sonication. The results show that the interaction between the solvent and the graphene can balance the energy required for the stripping of the graphene when the solvent surface can match the graphene, so that the graphene can be prepared by solvent stripping. Hamilton et al. [7] dispersed the graphene in o-dichlorobenzene and prepared monolayer graphene after ultrasonic dispersion. In addition, in order to increase the stability of the obtained graphene solution, it is often added some stabilizer during the solvent peeling to prevent the graphene sheet from being re-aggregated due to van der Waals forces. Englert et al. synthesized a novel amphiphilic substance and prepared it as a stable aqueous solution of graphene, which mainly utilizes the π-π stacking interaction between the material and the graphene sheet and hydrophobic effects. Hou et al.developed a monolayer and

multilayer graphene by the method of thermally intercalating the solvent in a highly polar organic solvent. The method mainly uses expanded graphite as raw material to disperse graphene by dipole-induced dipole interaction between graphene and acetonitrile.

In addition, the physical method of synthetic graphene also has the orientation epipass method, graphite intercalation method, arc method and so on. Because of the low cost graphite or expanded graphite as raw material, the preparation process does not involve chemical changes, micromachined stripping, thermal expansion and stripping grade solvent stripping method to prepare graphene has the advantages of low cost, high product quality and simple operation, but also exist Graphene yield is not high, graphene sheets easy to reunite and other defects, therefore, on the basis of the need to develop other methods of preparation of graphene better.

　3　Chemical vapor deposition

chemical vapor deposition　CVD is the process by which the reaction material is chemically reacted at a relatively high temperature and gaseous conditions, and the solid material is precipitated on the surface of the heated solid substrate to produce a solid material. Chemical vapor deposition method has been widely used in the purification of substances, the development of new crystals, deposition of various single crystal, polycrystalline or glassy inorganic film materials. It is also an effective method of synthetic graphene. Obraztsov et al. [8] and Kong et al. [9] made large-sized monolayer or multilayered graphene on the Ni substrate by chemical vapor deposition. This continuous graphene film material has a higher carrier mobility than micro-mechanically stripped graphene. However, it is not sufficient that the graphene material produced by the CVD method does not observe the quantum Hall effect exhibited by the graphene material obtained by the glass method. At the same time, the electronic properties of graphene by the substrate a great impact, it remains to be further studied.

（4）Oxidation - reduction method

Oxidation of graphite reduction method is the most commonly used method for the preparation of graphene, scientists at home and abroad have done a lot of research in this area. Graphite is a hydrophobic substance, compared to the oxidation of graphite

because of its surface and the edge of a large number of oxygen-containing functional groups, such as hydroxyl, carboxyl, epoxy, etc., is a hydrophilic material. The presence of these oxygen-containing functional groups makes the graphene oxide easier to react with other substances to obtain functionalized graphene. In addition, the intercalation layer of oxidized graphite is 0.7-1.2 nm, which is larger than the interval between graphite and 0.335 nm, which is favorable for the intercalation of other substances. At present, the preparation of graphite oxide method is usually used in the classic Hummers method.[10] The preparation principle is to use the first strong acid treatment of graphite, the graphite layer of the compound, then add a strong oxidant to oxidation. Oxidized graphite can be easily dispersed in water or organic solvent after appropriate ultrasonic treatment to form a uniform monolayer graphene solution, which is possible for people to prepare monolayer graphene. The method for preparing graphene from graphene reduction is chemical liquid phase method, thermal reduction method, microwave reduction method, light reduction method, solvent such as reduction method, especially in chemical liquid reduction. Commonly used reducing agents are hydrazine hydrate, $NaBH_4$, alkali, Fe powder, glucose, polyelectrolyte, dextran, ascorbic acid and so on.[11]

1.2 Introduction of heavy metal ions

Heavy metal ions are the corresponding ions of heavy metal elements. Heavy metals refer to metals with a specific gravity greater than 5 (generally referred to as metals with a density greater than 4.5 grams per cubic centimeter). Heavy metals refer to metals with atomic weights greater than 55. Such as iron atomic weight of 56, greater than 55, it is also heavy metals. There are about 45 heavy metals, generally belong to the transition element. Such as copper, lead, zinc, iron, cobalt, nickel, manganese, cadmium, mercury, tungsten, molybdenum, gold, silver and so on. Although heavy metals such as manganese, copper, and zinc are the trace elements needed for life activities, most heavy metals such as mercury, lead, and cadmium are not necessary for life activities, and all heavy metals are toxic to the human body. In addition, arsenic is not a heavy metal, but because of its sources and hazards are similar with heavy metals, it is usually included in the study of heavy metals to discuss.

In this article, I'm focus on detection of copper ions and silver ions

1.2.1 Introduction of copper ions

Copper ions are derived from two electrons whose copper atoms lose the outermost layer, are positively charged in the presence of hydrated ions [Cu (H$_2$O) $_4$] in aqueous solution. Cu^{2+} form exists, hydrated copper ions are blue, so our common copper salt solution is mostly blue.

Copper is a metal material that is widely used in people's production and living, and is also a major pollutant in the environment. But at the same time the copper element is also necessary for the animal and plant a trace of heavy metal elements, about 20 kinds of enzymes need to participate in the role of copper ions, such as cytochrome oxidase, superoxide dismutase, tyrosinase, lai aminoacyl oxidase and ceruloplasmin. However, when the content of copper ions in the body is too high, high concentrations of copper ions can damage and necrosis of cells, leading to organ dysfunction, so finding an effective method for detecting copper ions is still important.

Has many spectra of copper ions been reported in recent years, mostly based on light absorption or reflection. Although the fluorescence analysis method has the advantages of high sensitivity read, selectivity number, simple method and low sampling amount, there are some reports about the detection of copper ions by fluorescence method. But looking for new copper ion fluorescence sensors is still a hot field of research.[12]

1.2.2 Introduction of caffeine

Caffeine is a xanthine alkaloid compound, is a central nervous stimulant, can temporarily drive away sleep and restore energy, clinically used to treat neurasthenia and coma resuscitation. Caffeine is also the most commonly used psychotropic substance in the world, with coffee, tea, soft drinks and energy drinks that are caffeine.

Caffeine is a plant alkaloid that can be found in many plants. As a natural insecticide, it can paralyze insects containing caffeine plants. The most commonly used caffeine-containing plants in humans include coffee, tea and some cocoa. Other infrequent uses include Paraguayan holly and guarana trees that are commonly used to make tea or energy drinks. Two caffeine aliases: the Ma Dai and Guarana factors evolved from the two plants.

The world's most important source of caffeine is coffee beans (coffee tree seeds), while coffee beans are also coffee raw materials. Caffeine in coffee depends heavily on the variety of coffee beans and coffee production methods, and even the same tree in the coffee beans in the caffeine content is very different. In general, the amount of caffeine in a cup of coffee is from 40 milligrams of Arabian espresso to 100 milligrams in espresso. Deep roasted coffee is generally less caffeine than coffee, because roasting can reduce the caffeine content in coffee beans. Arab coffee caffeine content is usually lower than the fruit coffee. Coffee also contains trace amounts of theophylline, but does not contain theobromine.

Tea is another important source of caffeine, the caffeine content of each cup is usually only half the cup of coffee, depending on the strength of the tea. Specific varieties of tea, such as black tea and oolong tea, are higher than the caffeine content of other tea. The tea contains a small amount of theobromine and a higher theophylline than the coffee. The production of tea has a great impact on tea, but the color of tea is almost impossible to indicate the content of caffeine. Japanese green tea caffeine content is much lower than many black tea, such as Zhengshan race tea, almost without caffeine.

Chapter 2   Experimental materials and methods

2.1 Preparation of Fluorescent Oxidized Graphene

2.1.1 Chemicals

Graphene (8000 mesh), Phosphorus pentoxide made by Tianjin baishi chemical Co.Ltd, Potassium persulfate made by Tianjin Damao Chemical Reagent Factory, hydrogen peroxide (30%) made by Laiyang Kant Chemical Co.Ltd，potassium permanganate made by Shandong chemical Research Institute, ammonia, concentrated sulfuric acid (concentration 98%), hydrochloric acid (density 1.19%), copper sulfate made by Tianjin Chemical Reagent Factory III.

2.2.2 Preparation of Other Chemicals

Diluted hydrochloric acid (55 mL). Hydrochloric acid was added into water (volume of hydrochloric acid to volume water = 1:10).

Piranha solution (50 mL). Hydrogen peroxide was added into concentrated sulfuric acid slowly (volume of concentrated sulfuric to volume of 30% hydrogen peroxide = 7:3).

2.2.3 Oxidation

A. Pre-oxidation of graphene

5 g graphene (8000 mesh) was put into a 100 mL round bottom flask with a magnet. Then added 4 mL concentrated sulfuric acid (concentration 98%), 0.85 g potassium persulfate and 0.88 g phosphorus. After this the flask was put into oil bath which is in 80 ℃ and reacted continuously for 4.5 hours. When the reaction was done, the product was diluted by deionized water and dried for one day.

B. Primary Oxidation and Secondary Oxidation of graphene

Firstly added 0.5 g preoxidation product into 250 mL round bottom flask with a magnet.

Secondly, 2.5 g potassium permanganate (solid) was added and reacted for a while. During this process the round bottom flask should be put in ice bath, after which the round bottom should be taken out and reacted under room temperature for 2 hours. Then put it into water bath which was set under 35 ℃ and reacted also for 2 hours. After all of this, 41.5 mL deionized water should be added in order to dilute the solution. After 2 hours added 116.5 mL deionized water and 3.3 mL hydrogen peroxide slowly, the solution would be turned to yellow and continued stir and react for 2 hours.

After reaction, the diluted hydrochloric acid was mixed with product solution. Then the mixed solution should be centrifuged at least 6 times until the PH went to 7.

We got the nanoscale graphene when primary oxidation was done, then it was time to do secondary oxidation of graphene.

Prepared three centrifuges firstly. Then added primary oxidation product 2 mL into a centrifuge tube, repeated 2 times other two centrifuge tubes. 6 mL piranhas was separately and evenly added into 3 centrifuges for reaction. Three centrifuge were marked on No.1 and No.2. No.1 reacted for 1 hour, No.2 reacted for 8 hours. When reaction was done, the supernatant should be taken while the precipitate was retained. The precipitation was the fluorescent oxide graphene.

Figure 2-1: Product of Fluorescent Oxide

Chapter 3   Characterization

3.1 Fluorescence Spectroscopy

After oxidation the oxidized graphene was detected by fluorescence spectroscopy and got figure 3-1. Figure 3-1 shows that though the fluorescence intensity is weak, the fluorescence will decrease after adding copper ions. This sample is secondary oxide for 8 hours and dialyed for 9 days after oxidation.
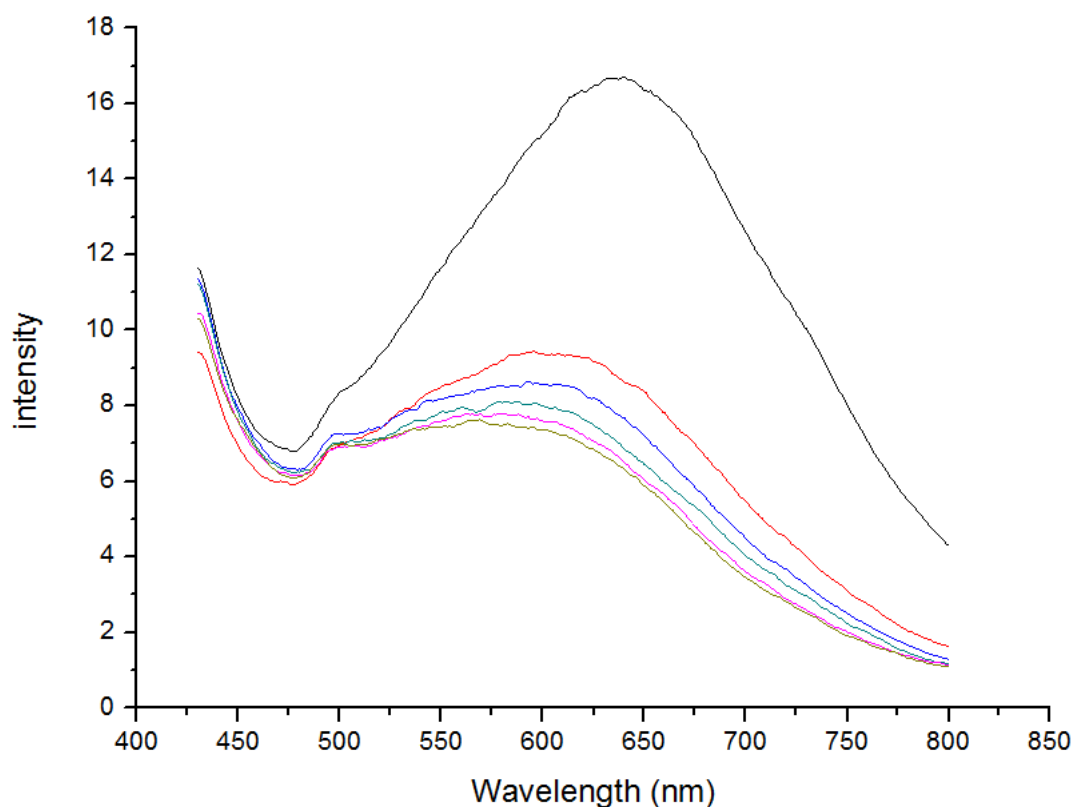

Figure 3-1: Graph of Cu^{2+} Fluorescent Spectroscopy (8 h and 9 days dialysis)

In this figure, different color of lines means different amount of added copper sulfate. Black line (oxidized graphene), red line (oxidized graphene with 10 µl 0.01 mol/L CuSO$_4$), blue line (oxidized graphene with 20 µl 0.01 mol/L CuSO$_4$), green line (oxidized graphene with 30 µl 0.01 mol/L CuSO$_4$), pink line (oxidized graphene with 40 µl 0.01 mol/L CuSO$_4$) yellow line (oxidized graphene with 50 µl 0.01 mol/L CuSO$_4$) From black line to yellow line, the peak is lower and lower as the amount of copper ions increase. (Figure 3-2)
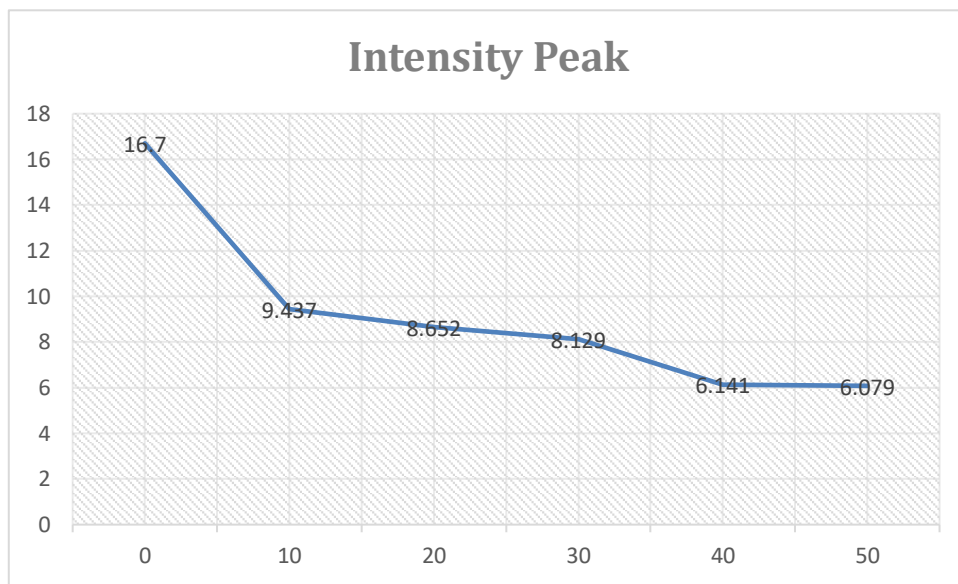

Figure 3-2: Trend of Intensity Peak (8 h and 9 days dialysis)

According to Stern-volmer equation $F_0/F=1+K[Q]$ (F_0 represents the intensity of fluorescent oxide graphene which is not added copper ions, F represents the intensity of fluorescent oxide graphene which is added copper ions, Q is the concentration of copper ions and K is quenching constant.)

When F_0=16.700, F=9 .437, Q=0.01 mol/L, K_1=77.

When F_0=9.437, F=8.652, Q=0.01 mol/L, K_2=9.1

When F_0=8.652, F=8.129, Q=0.01 mol/L, K_3=6.4

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In order to prove the influence of reaction time, I also tested oxidized graphene which was just reacted for 1 hour. (Figure 3-3)

In this figure, different color of lines also means different amount of added copper sulfate. The meaning of different lines are the same with the last graph.
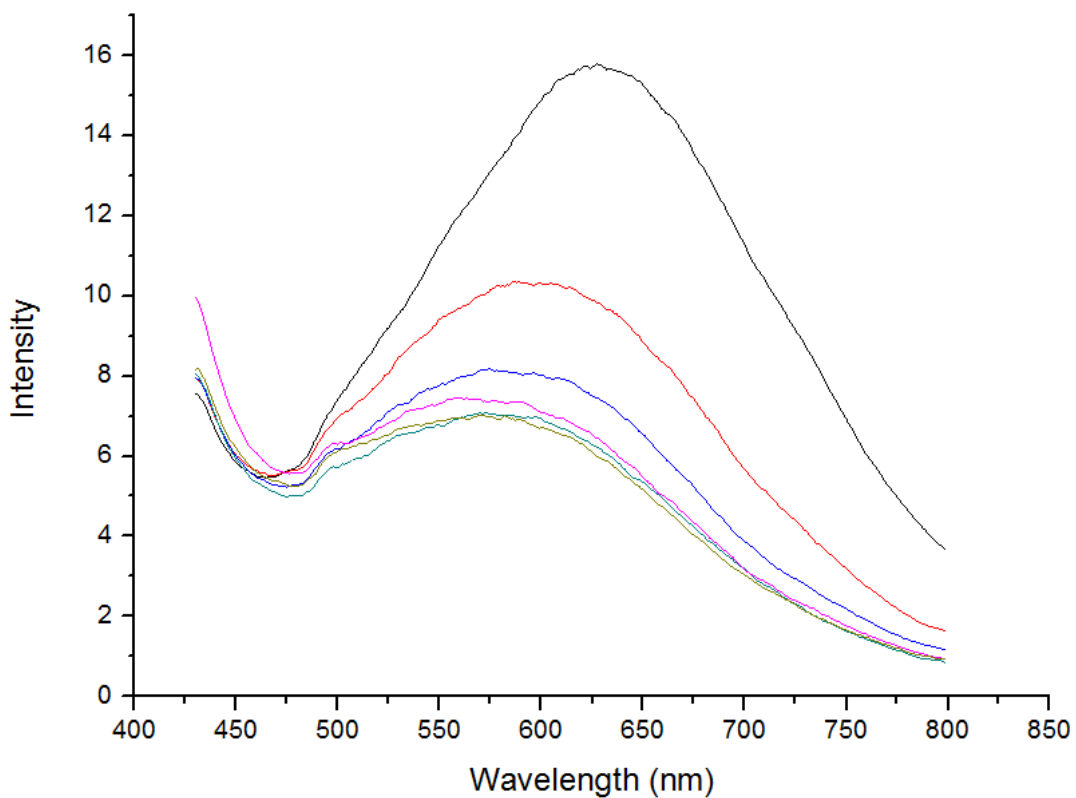

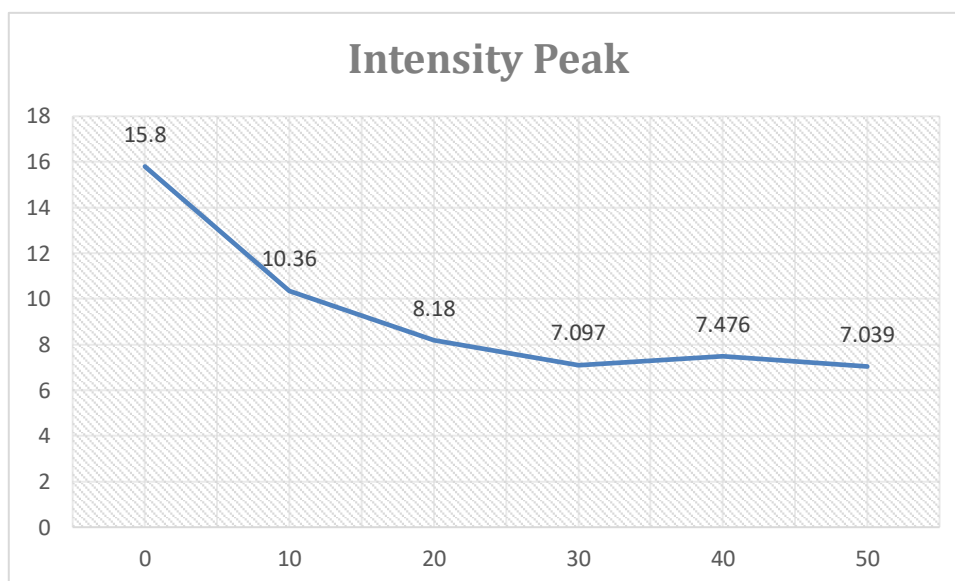Figure 3-3: Graph of Cu^{2+} Fluorescent Graphene (1h and 9 days dialysis)

Figure 3-4: Trend of Intensity (1 h and 9 days dialysis)

The trend is almost the same with the former one. (Figure 3-4)

According to Stern-volmer equation $F_0/F=1+K[Q]$.

When $F_0=15.80$, $F=10.36$, $Q=0.01$ mol/L, $K_1=52.5$

When $F_0=10.36$, $F=8.18$, $Q=0.01$ mol/L, $K_2=26.7$
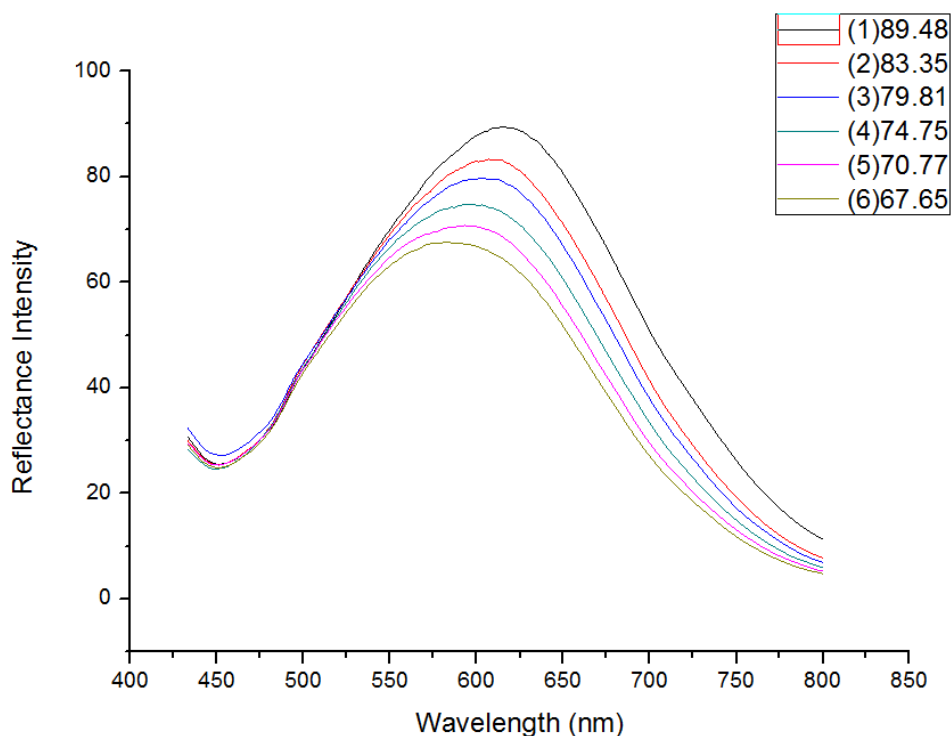
When $F_0=8.180$, $F=7.097$, $Q=0.01$ mol/L, $K_3=15.3$

Figure 3-5: Intensity of Cu^{2+} Fluorescent oxide graphene (No dialysis)

In order to find is there any influence caused by dialysis, we prepared samples without dialysis. From this graph we can see that the intensity of fluorescence is much higher than samples with 9 days dialysis.

There is another alkaline matter exists in tea which is caffeine. To test is there any influence to fluorescence by caffeine, we also did a fluorescence test with caffeine.

The concentration of caffeine is 0.01 mol/L which has no difference with $CuSO_4$ solution we prepared in former. The fluorescent oxide graphene we prepared has no dialysis.

We added caffeine as volume 10 µl, 20 µl, 30 µl, 40 µl and 50 µl respectively, then we got the graph below (Figure 3-6).
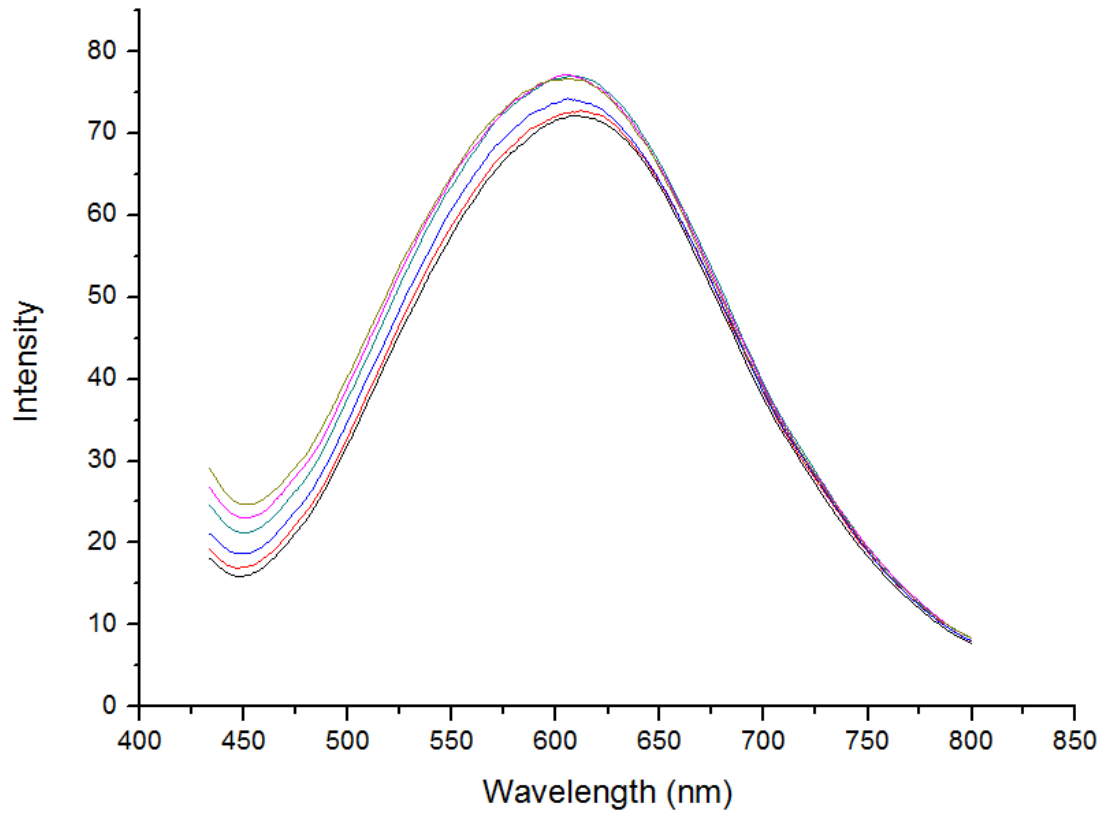
Figure 3-6: Intensity of caffeine Fluorescent oxide graphene

In this graph, there is almost no change when we added caffeine inside solution of fluorescent oxide graphene.

Chapter 4   Conclusion

In this experiment, under 365 nm UV lamp, the fluorescence oxidized graphene absorbs lights except red light, which means we can see the fluorescence oxidized graphene is orange under UV lamp (The wavelength curve peak is around 650).

To conclusion, the copper ions really have the ability to quench fluorescence which comes from fluorescent oxide graphene. It can decrease the intensity of fluorescence, which means heavy metal ions have the ability to decrease the intensity of fluorescence comes from fluorescent oxide graphene.

Fluorescent oxide graphene which oxided for 8 hours is much easier to be quenched by copper ions comparing with fluorescent oxide graphene which oxided for 1 hour. Which means the test line of fluorescent oxide graphene (8 hours) is much lower than the test line of fluorescent oxide graphene (1 hour).

After 9 days dialysis, the intensity of fluorescence decrease significantly. But it is much more sensitive when meets copper ions. Because before the dialysis, there are lots of impurities in fluorescent oxide graphene solution. The phenomenon of fluorescence quench is hard to happen when there are lots of impurities exist. After dialysis, impurities go out and only fluorescent oxide graphene exist in solution. So samples which have 9 days dialysis have such low test line.

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