



齊魯工業大學
QILU UNIVERSITY OF TECHNOLOGY

本科毕业论文

Study on the Optical Responsiveness of
Carbon Dots to Organic Amines

学院名称 化学与制药工程学院
专业班级 16-1 应用化学（国际班）
学生姓名 王凤阳
学 号 201604301341
导师姓名 迟虹

2020年06月08日

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碳量子点对有机胺的光学响应性研究

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学生姓名 王凤阳
学号 201604301341
导师姓名 迟虹
专业技术职务 副教授

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毕业设计（论文）作者签名： 王凤臣

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Abstract

Carbon dots(CDs) is an advanced new carbon-based nanomaterial, which has an excellent performance in microimaging, biosensing, chemical sensing, and catalysis. In recent years, food poisoning incidents caused by organic amines exceeding the standard in seafood are common. Numerous studies have shown that putrescine is the most common organic amine in corrupt seafood and is highly toxic, threatening human life and health. In order to give full play to the excellent chemical sensing capability of CDs, this study applies CDs synthesized from raw materials such as o-Phenylenediamine (OPD) to the sensing of organic amines and studies the sensing performance of CDs in the optical signal. At room temperature (35% -40% relative humidity), putrescine is easy to combine with water molecules in the air to produce a smoke effect. As the homemade CDs film in contact with the combination and produce significant color changes, the dark blue area immediately shallow, thus judging the presence of putrescine. Because the response mechanism is simple and clear, the optical signal is clear and easy to judge, the response is quick and does not require professional and technical support, so this response mechanism can be applied in the aquaculture and other fields, which helps to reduce the threat caused by corrupt seafood, and protect people's lives and health.

Key words: Putrescine; Carbon dots; Optical signal; Aquatic products; Chemosensor.

摘要

碳点是一种先进的新型碳基纳米材料，其在生物显微成像、生物传感、化学传感、以及催化等方面具有十分优秀的性能表现。而近年来因海产品中生物胺超标而引起的食物中毒事件屡见不鲜。大量研究表明，腐胺为腐败海产品中最常见生物胺，且有剧毒，对人类生命健康造成威胁。为发挥碳点出色的化学传感能力，本研究将利用邻苯二胺等原料合成的碳点应用到有机胺的传感当中，研究碳点对生物胺在光学信号传感上的表现。在室温条件下（相对湿度 35% -40%），腐胺易与空气中水分子结合产生发烟效果，自制碳点薄膜在与之接触后产生明显的颜色变化，深蓝色区域立刻变浅，由此判断腐胺存在。由于响应机理简单明了，光学信号清晰易判，响应迅速且无需专业技术支持，因此该响应机制在水产品等领域具有一定的应用前景，有助于减轻腐败海产品带来的威胁，保护人民生命健康。

关键词：腐胺 碳量子点 光学信号 水产品 化学传

Chapter 1 Introduction

1.1 Detection methods for organic amines

The initial idea of our research comes from the aquatic products food poisoning. Nowadays, aquatic products have been an important nutrient source for human beings, it's an indispensable part of Chinese cuisine and customs. However, the decay of aquatic products is a serious problem for this industry. For so many years, food poisoning that caused by rotten aquatic products are quite common in our life, but there are no simple and easily accessible methods to test the freshness of aquatic products. In this work, through reviewing literature related to aquatic products, and find that rotten aquatic products usually release some organic amines like putrescine, cadaverine, histamine, and tyramine, and putrescine is the most common one [1]. Compared with detecting the freshness of aquatic products, figure out how much of the food has rotten is much easier. Putrescine is assumed to be an important chemical that can affect the pH value inside cells. However, it is also been recognized as a kind of highly toxic organic amine, only dozens PPM of it can cause faint, it is also toxic in contact with skin, which may cause skin burns and severe eye damage. So it's necessary to develop a simple and cheap putrescine detection method to avoid the common occurrence of food poisoning incidents. By now, chromatography is still a reliable way to detect organic amines, such as HPLC, IC, and even GC-MS. Some scientists tried to use ELISA to detect amines, they immobilize histamine dehydrogenase and putrescine oxidase on working screen-printed electrodes by enzyme crosslinking, this way, the number of amines can be calculated by the measuring the oxidation current of the mediator on each electrode. But all of these methods above must be operated with the suspension liquid of samples, the samples preparation is a time-consuming process.

Henao-Escobar et al. [2] immobilize histamine dehydrogenase and putrescine oxidase on working screen-printed electrodes by enzyme crosslinking, this way, the number of amines can be calculated by the measuring the oxidation current of the mediator on each electrode. This dual system can detect the amount of histamine and putrescine at the same time, the limit of detection for histamine is $8.1 \pm 0.7 \mu\text{M}$, and $10 \pm 0.6 \mu\text{M}$ for putrescine. However, the organic amines were detected in prepared solutions, it is still not as simple as the test paper like pH test strips. There is no easily

available putrescine detection method based on the optical signal, and it is unrealistic for common people to prepare a sample suspension solution for the freshness evaluation of aquatic products. In the study of Hong Chi et al. [3] . They reported the humidity sensing performance of GO that based on the optical signal and showed a surprising result that the spectra changes can exactly be noticed by naked human eyes, which initiated a new idea for the sensing application of GO materials. By now, there are so many studies which trying to develop the sensing application of GO, like the electric facilities that based on modified GO materials, bio sensing and so on, which has been a hot topic in the last few years.

Ravi Kumar et al. [4] developed an ammonia gas sensor based on functionalized GO, the Langmuir Blodget tech was introduced to generate GO thin film on Silicon wafers, and the Meta Toluic acid(MTA) solutions with different concentrations were used for the functionalization of GO thin film, this process relies on the esterification reaction between GO and MTA, it exhibited excellent stability and sensing performance after three cycles of gas exposure. In this work, MTA worked as the substance that trapping ammonia gas molecules on the surface of the modified GO film. The sensing process carried out with gas injection and I/V measurement equipment, which means the sensing still relies on the variation of resistance of modified GO film.

Of course the MTA which was mentioned above can be changed in order to apply this sensing mechanism to the other substance except ammonia gas. However, this sensing performance is not clear enough according to the published paper. More specific studies have to be finished in this study. But there's no doubt that it opened a way for later research. The FTIR diagram proved the existence of the ester group, Raman spectroscopy confirmed the increase of defects sites, In this case, ammonia gas molecules may interact with the oxygen atom of the ester group through hydrogen bonding of the H atom of NH₃, forming H₂NH-O bonding configuration. Dissociated NH₃ molecules may be absorbed at these sites and form the sigma bonds with carbon atoms.

In the present case, the epoxide ring present at the GO surface plays a crucial role in NH₃ gas sensing. The opening of the epoxide ring may create oxygen and carbon sites. There are two possible ways for the opening of the epoxide ring at GO surface. One is, epoxide ring present at the GO surface may break during functionalization. Another possibility for the same is during the dissociation of NH₃ molecules as while interacting with sensing film, NH₃ gas molecules may dissociate into NH₂ and H. In

both above-mentioned cases, the dissociated NH_2 and H molecules may get chemisorbed on available carbon and oxygen sites results in the formation of chemisorbed OH and NH_2 molecule. The last possibility is physical absorption, gas molecules just simply been trapped by the functionalized GO structure.

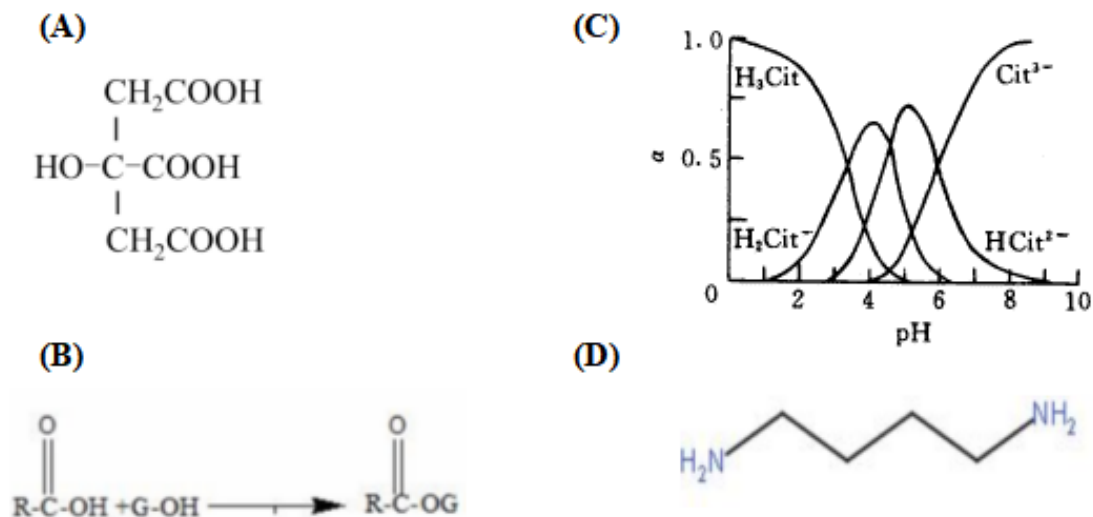


Figure 1. (A) Molecule formula of Citric acid; (B) Esterification reaction [4]. ; (C) Citric acid ionization diagram; (D) Molecule formula of putrescine.

1.2 Comparison between GO and CDs

In the last few years, the colorimetric sensors based on nano materials thin film have been a hot topic. It is well known that GO is assumed to be a single atomic layer [5]. Due to the distribution of functional groups like hydroxy and epoxy groups on the surface of GO, and the carboxyl and carbonyl groups on the edge, GO exhibits excellent hydrophilia and dispersion property in water. Therefore, a very beautiful GO thin film can be obtained through coating GO aqueous suspension on the surface of a hydrophilic treated silicon wafer with the help of a spin coater. However, it is far from enough with only a thin GO film, the high-impedance state also limited the electrochemical development of this material (square resistance reaches $10^{12} \Omega \cdot \text{sq}^{-1}$) [6].

In other words, although GO is an excellent choice for the colorimetric sensor, there are still various materials waiting for us to try. Such as single-wall nanotubes (SWNTs), carbon dots (CDs), polymeric materials and so on. Due to the great expression on the optical property and relatively small size (less than 10 nm) of carbon dots [7], a novel material was firstly reported by Xu Xiaoyou et al. in 2004. It can be applied to our colorimetric sensor. CDs have good dispersion property in water just like GO, and also eco-friendly, owns good bio-compatibility. At this point, the property of

this carbon-based material looks just like GO, but with better fluorescent and optical properties. The main fluorescent peak of CDs is concentrated in the wavelength from 260nm to 320nm, thus it has been widely used in bio-sensor, bio-imaging, and catalyzing. Jingfang Shangguan et al. [8] reported the first use of a novel kind of label-free carbon dots for intracellular ratiometric fluorescence pH sensing, the CDs was synthesized simply by one-pot hydrothermal treatment of citric acid and basic fuchsin, the product shows dual emission band at 475 and 545nm. We also expect the fluorescent emission can be seen in our self-prepared CDs.

Liang Wang et al. [9] reported a dual-mode colorimetric/fluorescent sensor that was fabricated from CDs, it provides a way to determine pH value under visible light and fluorescent condition. In visible light, the color of the CDs-loaded filter paper is different under different pH value, it's purple to light yellow from the pH value of 1 to 14. In a similar way, under the UV light, the color varies from red to yellow as pH value changes from 1 to 14, and the fluorescence tends to disappear at extreme acidic/base conditions.

This CDs was synthesized through the one-pot hydrothermal method. Raw materials consist of 1,2,4-triaminobenzene and NaOH. Carbon and nitrogen was provided by the 1,2,4-triaminobenzene. And the NaOH worked as a catalyst for 1,2,4-triaminobenzene molecular fusion, and further to ensure the oxygen doping. There are plenty of $-OH$, $-NH_2$, $N-C$, $N-O$, and $C=O$ groups on the surface of the CDs products, XPS diagram proved the existence of functional groups like $-COOH$, $-N-OH$, NH_2 on the surface of CDs. As a carbon-based zero-dimensional material, which has such a proper size(0.4-2.6nm), CDs can attach more functional groups than it's close relative-graphene oxides, SWNTs, carbon nanofibers and so on. Furthermore, the carboxyl groups on CDs might be useful for our research, due to the interaction between $-COOH$ and putrescine, there will be a slightly different with CDs' structure, and then it may have an impact on the color of our self-prepared CDs thin film, which could be quite interesting like the filter paper below, a possible opportunity to develop a novel seafood freshness detector.

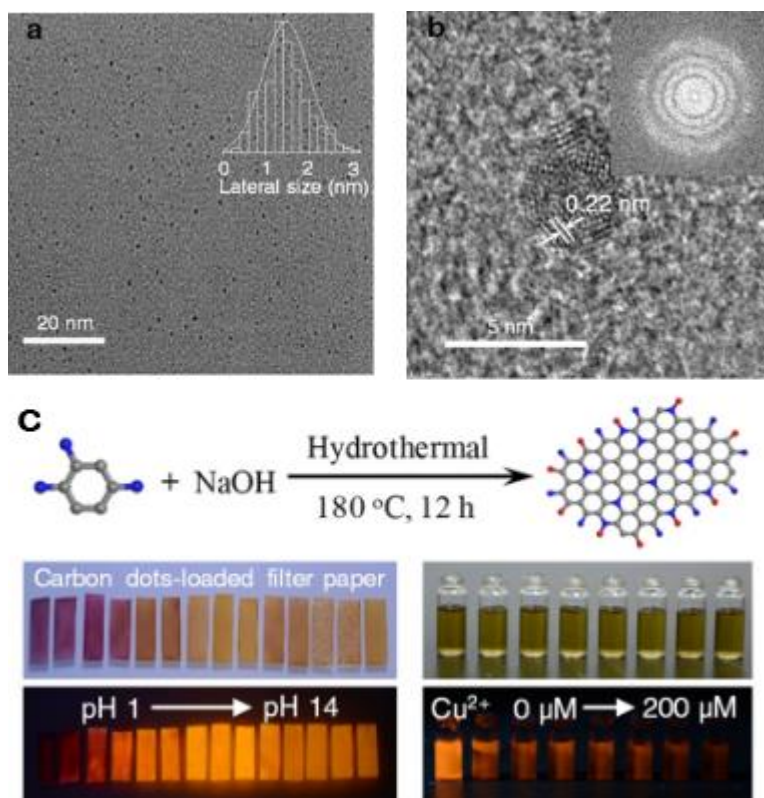


Figure 2. (a) Lateral size distributions and TEM images of CDs; (b) High-resolution TEM images of CDs; (c) Synthesis and sensing performance of the CDs [9].

1.3 Strength of colorimetric methods compared with electric

Color has always been a powerful tool since ancient times. For example, the brightly painted mushrooms are mostly toxic, pale and sallow skin often means a man under sub-health condition. Even it is already in twenty-first century now, it is still a rather important role in our society. For example, red and green are universal indicators for respectively stop/danger and go/safety, as well the wide usage of pH test strips. So it means the optical is more user-friendly, and it doesn't matter if there's the electromagnetic interference or losing power. Because there's no business with electric, the production of this sensor is also relatively easier. It's the simplest way to transmit information, and people can recognize optical signal more intuitively than some other way. In summary, it's a better choice to operate large-scale detection and production with an optical sensor[10].

As the fast development of science and technology goes on, now there are more advanced and smart colorimetric sensors. For example, Michael C. Janzen et al. [11] reported a colorimetric sensor array for VOCs more than a decade ago. The array was made from chemo-responsive dyes and then imaging through a usual scanner. A simple detection method, but owns powerful identification capability. It can distinguish plenty

of closely related organic compounds, like some aldehyde, alcohol, organic acid, benzene series and so on. Besides, the effects of humidity on this sensor are relatively small, essentially non-responsive on humidity changes.

The GO humidity sensor study of Bo Liu et al. [12] also relies on the electronic signal, but the way to process the electrode is quite useful to our research, the spin-coating. The study is based on a gas-sensitive test system(WS-30A) and converted Ag-Pd interdigital electrode, they dripped the graphene water dispersion on the surface of the electrode, and then let it dry through rotation and heating. The sensor response was obtained through the resistance changes while sampling voltage was 5V. Compared with the Langmuir Blodgett tech, spin coating is an easily available coating method, it is suitable for the surface coating process in the fields like microelectronics, semiconductor, optical devices, plate making, new energy, biomaterials, its working principle based on a high speed rotating substrate, which using the centrifugal force to coat the coating drops evenly on the substrate, the thickness of film depends on the amount, concentration, viscosity of coating drops, it is also related to rotational speed and time.

Furthermore, except for the colorimetric signal, there are still some other optical signals like the infrared and fluorescent signal. Jingfang Shangguan et al. [8] developed CDs-based fluorescent pH nanoprobe for intracellular pH sensing. When applying basic fuchsin and citric acid in a molar ratio of 1:1000 to synthesis CDs, the products show an excellent and stable fluorescent performance. The fluorescence intensity ratio ($I_{475\text{ nm}}/I_{545\text{ nm}}$) of the carbon dots was linear against pH variation and has a good linear relationship against pH values from 5.2 to 8.8 in the buffer solution.

However, organic amines are quite different from ammonia and water, most of them are liquid or solid under room temperature, like putrescine, melting point varies from 25°C-28°C, typical volatile organic compounds(VOCs). So it is rather important to control the volatilization of putrescine [13]. Hosang Ahn et al. [14] controlled the concentration of ethanol gas by creating an environment that contains flowing self-mixed gases, which includes oxygen(20sccm), pure nitrogen, and ethanol(500ppm) gases, then they get the ethanol concentration with an equation

$$C_{\text{ethanol}}(\text{ppm}) = \frac{500 \times MFC_1}{MFC_1 + MFC_2 + MFC_3}$$

MFC_3 (80~0sccm) exhibits ethanol cylinder's flow amount, MFC_2 (20sccm) is the amount of O₂ gas, MFC_3 (0~80sccm) represents the amount of N₂ gas.

And the content above related to the equation was accomplished by the gas mixing system below. This feasible detection method of ethanol gas, which based on the electric signal of ZnO nanorods. Sensing properties were characterized by recording the resistance change of ZnO nanorods as a function of ethanol concentration in synthetic air and working temperature. The sensing performance of the nanorods is characterized by recording the resistance of zinc oxide nanorods in the synthetic air with changes in ethanol concentration and operating temperature. At the point of sensitivity, it's sensing performance is far better than the ZnO nanorod sensors fabricated on a silicon dioxide hard substrate [14].

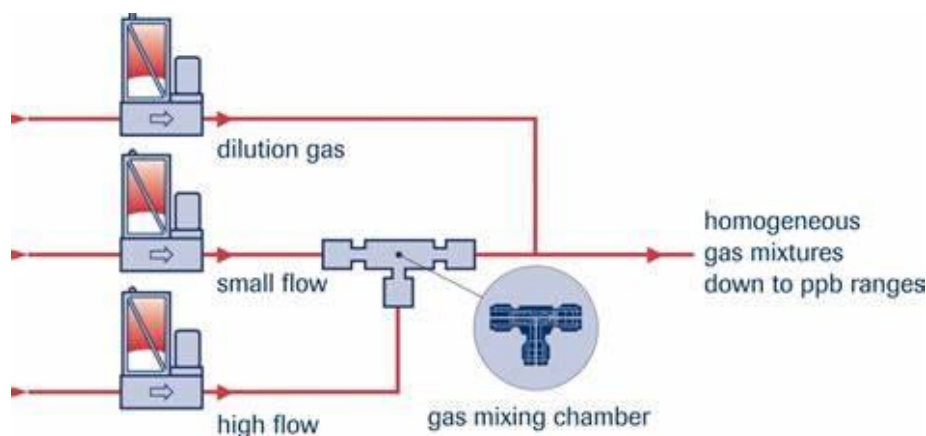


Figure 3. Gas mixing system [14].

1.4 The synthesis of CDs

Peerasak Paoprasert et al. [15] prepared carbon dots(CDs)from black sesame through the one-step hydrothermal method. They introduced the self-made CDs to the electronic nose system. The optical-electronic nose system consists of light sources, sensing materials, and a photodetector. LEDs and a commercial photodetector(ET-TCS230) were used to detect light intensity. The eight gas sensor arrays were generated based on eight colors of LEDs. The transmitting light intensity through sensing thin film was observed in the form of photon frequency(Hz), captured by a photo-detector. Ammonia, triethylamine, and ethylenediamine were used for the detection test. The results of light transmission show a different signal for different amines, but the limited description can not simply support this theory. Based on this result, we'd better try a more reliable method to detect organic amines.

Except for black sesame, there are various raw materials that can be used in the synthesis of CDs. Syamantak Khan et al. [16] prepared their bio-imaging CDs with urea and citric acid by solvothermal method, the CDs synthesized with citric acid are known

to be non-toxic, it also shows better bio-compatibility compared with many commercial fluorescent probes. Li Wang and H. Susan Zhou [17] reported another green synthesis method for luminescent N-doped CDs. Stirring the mixture of 20ml water and 25ml milk violently, then add it into the autoclave reactor to react for 2 hours at the temperature of 180°C, then the particles were filtered through 0.22 μm Millipore syringe filters before the use. Prepared CDs have almost no cytotoxicity. It can be effectively taken up by human U87 cells.

There are many methods used to prepare CDs, making it an important consideration along with the choice of the precursor. Hydrothermal methods are popular because of the high availability and “green” nature of water. These methods will commonly heat up to between 160 and 200 $^{\circ}\text{C}$ in a sealed autoclave or with a reflux condenser. The resulting CDs are attractive because the method ensures that they will have high water dispersibility and oxygen-containing functionalities [18].

Chapter 2 Experimental Section

2.1 Reagents and apparatus

2.1.1 Reagents

Table 1. Reagents used in this experiment.

Reagents	Purity	Manufacturer
1,4-Diaminobutane	98%	Shanghai Aladdin Bio-Chem Technology Co., LTD
Calcium chloride anhydrous	99.9% Metals basis	Shanghai Aladdin Bio-Chem Technology Co., LTD
o-Phenylenediamine (OPD)	99.5%	Shanghai Macklin Biochemical Co., Ltd
Ethanol	AR,99.7%	Shanghai Macklin Biochemical Co., Ltd
Ethylene glycol	AR,98%	Shanghai Aladdin Bio-Chem Technology Co., LTD
Potassium hydroxide	GR,95%	Shanghai Aladdin Bio-Chem Technology Co., LTD
Magnesium sulfate	99.99%	Beijing Mreda Technology Co., Ltd.
N-propanol	99.5%	Shanghai Aladdin Bio-Chem Technology Co., LTD
Isopropyl-alcohol	HPLC,99.8%	Shanghai Macklin Biochemical Co., Ltd
Acetone	98%	Shanghai Aladdin Bio-Chem Technology Co., LTD
Silicon wafer		Zhejianglijing Technology Co., Ltd
H ₂ O ₂ solution	30%	Beijing Mreda Technology Co., Ltd.
Concentrated H ₂ SO ₄	98%	Shanghai Macklin Biochemical Co., Ltd

2.1.2 Apparatus

Table 2. Instruments used in this experiment.

Name	Model	Manufacturer
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Magnetic Stirring Oil Bath	DF-101S	Gongyi City Yingxia Instrument Factory
Water Purification System	UPT-II	Xi'an Youpu Instrument Equipment Co., Ltd.
Finnpipette	F3	Thermo Fisher Scientific
Transmission Electron Microscope (TEM)	JEM-2100	JEOL
Teflon autoclave	—	—
Ultrasonic bath	—	—
Spin coater	EZ4	Schwan Technology Co., Ltd.

2.2 Experimental materials' preparation

2.2.1 Synthesis of CDs

The CDs were synthesized by a one-pot hydrothermal way using 0.3 g o-Phenylenediamine (OPD), 30 ml ethanol, and 2 ml ethylene glycol. In the beginning, 0.3 g OPD was dissolved in 30 ml ethanol, and then 2 ml ethylene glycol was added to the solution, then transfer it into a 50 ml Teflon autoclave. After heating at 180 °C for 8 hours, cool down the autoclave to room temperature, then the solution that contains well-dispersed CDs is obtained.

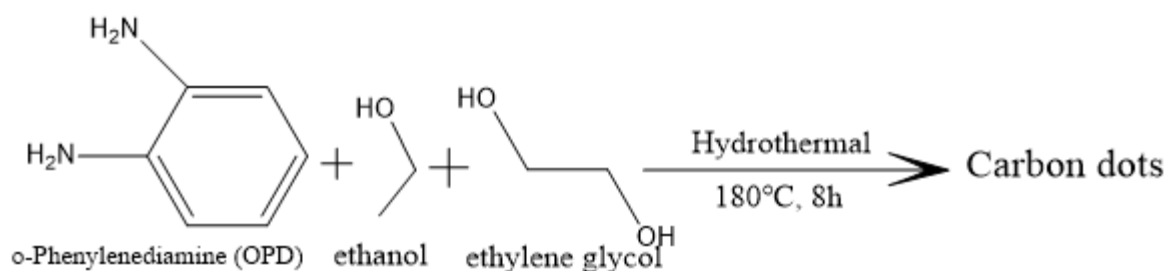


Figure 4. Synthesis formula of CDs.

2.2.2 Hydrophilic treatment and cleaning to the silicon wafer

Before starting the hydrophilic treatment, it's very important to clean the silicon wafer first. Three solvents were used in this process, put the silicon wafer into n-propanol, isopropyl-alcohol and acetone solutions respectively in the ultrasonic bath for 5 minutes, and then clean them with ultrapure water for five times.

Cleaned silicon wafers were treated with piranha solution, which contains 5ml

H₂O₂ solution(30%), and 15ml concentrated H₂SO₄ solution(98%), V_{H₂O₂}: V_{H₂SO₄}=1:3. After putting the silicon wafer into the mixed solution, the solution was heated at 110 °C for an hour, then cool down the solution to room temperature. Take silicon wafers out, and clean them with ultrapure water for five times. Finally, the silicon wafers which owns a much better hydrophilia property was obtained.

2.3 Spin coating

The spin coater below was used for CDs thin film coating. The coating process contains four steps which have different coating speed and time, our setting is 200 rpm, 1 min →500 rpm, 1 min →2000 rpm, 5 min →500 rpm, 10 min. The purpose of the first step is to let the CDs solution drops evenly distribute on the silicon wafer, and then thinner the film through increase the rotation speed and time, to dry the thin film, let it rotate at 500 rpm for 10 minutes in the end.

The CDs solution was diluted to 1.5 mg/ml, and it's so dilute that the coating process needs to be repeated for ten times before getting a proper CDs film. However, it's the only way out, because when the origin CDs solution was coated on the surface of silicon wafer, the liquid which spread quite uniformly just can not be dried quickly, the drying process usually took a day time to complete. Besides, after drying, there's another problem that the film is so thick that the abundant color can not be observed on the film anymore, what left was only the sticky brown CDs, which can not tell any differences on visible light or fluorescent signal. So the coating solution must be diluted enough to form a uniform and beautiful CDs film, although it may take a long period of time. Slow work yields fine products.

Nonetheless, the finest coated CDs film is still not good enough. As the Figure 6.(B) demonstrate below, although the rich color of the film is very clear, no matter the yellow, red, blue, or purple. It also exhibited an excellent color change as the breath was blown onto it, the yellow area turned to red, and the blue and purple area seems been bleached, the color became shallow. In the meantime, the thick brown area has no response at all, which expresses the importance of solution concentration, as well the difficulty of forming a beautiful CDs film which has a uniform thickness and color. Thus, this study opened the way for the later studies, but there are so many contents needs to be systematically studied.

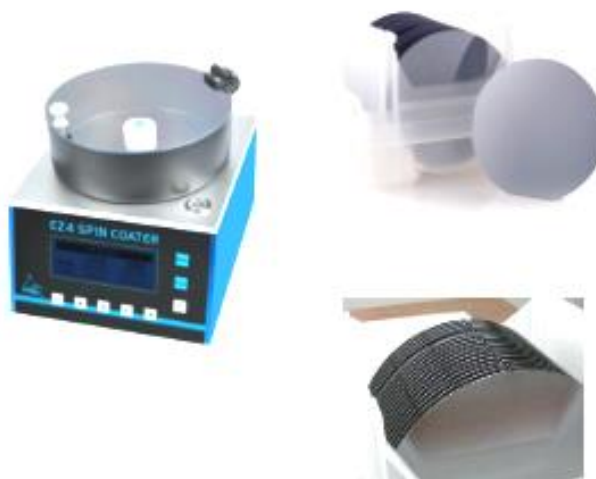


Figure 5. Spin coater and silicon wafer.

2.4 Sensing capability verification

At the beginning of this work, an injector was simply used to blow putrescine vapor on the surface of the CDs film, and it did show a rapid color change. As the picture below shows, the dark blue/purple area on the left turned to reseda after blowing putrescine vapor on the surface, because it shows the same phenomena when people breathed on it, and putrescine is highly soluble in water. So it might be affected by H_2O molecules in the air, which might combine with putrescine molecules while we were testing, then show the color change below.

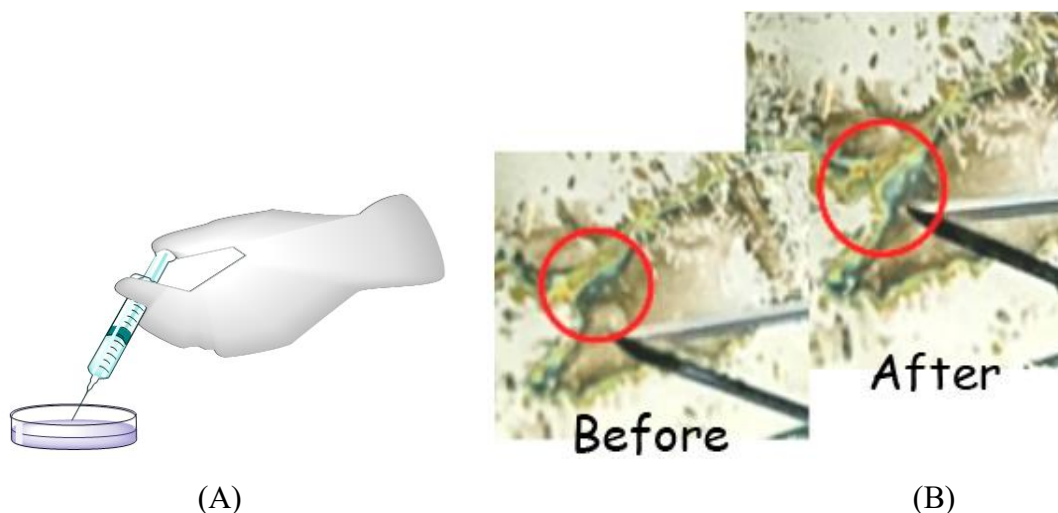


Figure 6. (A) Testing schematic diagram; (B) Color change after blowing putrescine on the film.

In order to remove the influence that causes by water molecules, another sensing system just like the schematic diagram below was designed, which contains three parts: temperature control, gas dryer, and the data collecting. As the N_2 gas blowing through the system, putrescine vapor in the three-necked flask was pushed through the drying tube, which absorbed the water molecule in the gas. The dry putrescine vapor then finally reaches the silicon wafer which was place in the transparent PMMA box, a camera at the end is responsible for data collection.

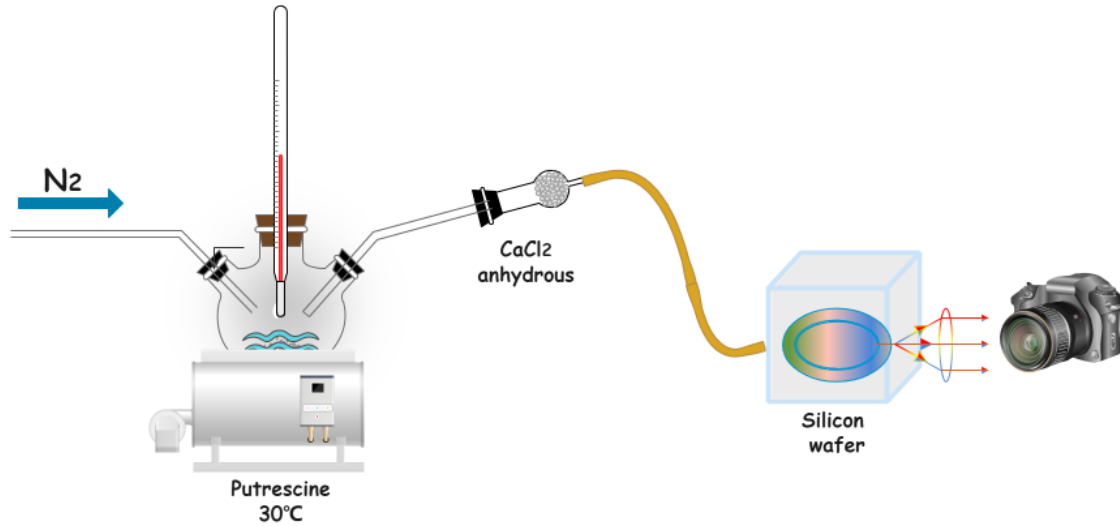


Figure 7. Sensing system schematic diagram.

Chapter 3 Results and Discussion

3.1 Characterization of CDs

3.1.1 TEM image of CDs

According to the TEM image, the size of our self-prepared CDs ranging from 5 nm to 15 nm, and it has great dispersity in the solution.

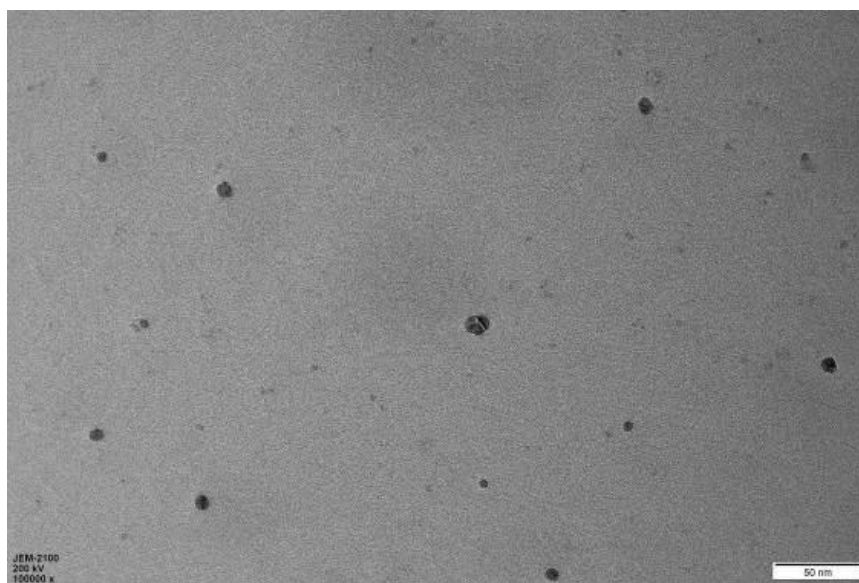


Figure 8. TEM image of the self-prepared CDs.

3.2 Sensing performance of the CDs film

According to the experiment's result, at room temperature (25 °C), relative humidity varies from 35% ~ 40%, which is quite familiar to the environment around seafood. The CDs film has nothing changed at all when the air was blown onto it, but it shows clear color changes as the putrescine was blown onto the surface of the film, the dark blue area turned into wathet blue instantly.

However, after removing the water molecules in the air, the sensing performance just vanished in the air. One reason is that the putrescine molecules can not combine with the water molecules after the applying of the drying tube. Then the putrescine might be blocked by the drying tube, but the unique odor of putrescine still can be smelt as the silicon wafer was taking out of the box. So it's clear that the putrescine did go through the experimental unit successfully.

Thus, here the conclusion can be drawn that the thin CDs film that prepared in this research has the ability to identify putrescine in room temperature(25 °C, RH: 35% ~ 40%), which means it is possible to apply this colorimetric identification method to our life. Because the visualized operation is very easy and simple, it doesn't require any specific technical support, naked-eyes can straightly observe the sensing process as it only contains visible light signal.

However, unfortunately, due to the effect of the pandemic caused by COVID-19, it's not possible to continue the experiment to take more detailed research. This study proved that the self-prepared CDs thin film can be used for the detection of organic amines like putrescine, and shows a clear visible light signal.

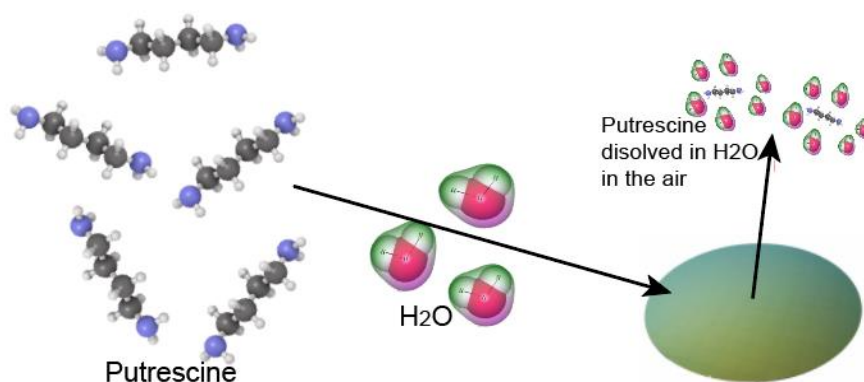


Figure 9. Sensing mechanism.

3.3 Difficulties in the research

In this study, the most important work is the spin coating, film coating is the most challenging process. Although it's just repetitive work, nothing abstract and complicated. Producing a perfect CDs film on the silicon wafer is still like a fantasy. The picture of these failed samples below can tell it perfectly.

There are several items which may affect the general appearance of the film. The cleaning and hydrophilic treatment of silicon wafers are rather important. In other words, the CDs particle can not attach to the silicon wafer if the substance haven't been treated properly. Then the liquid which was dropped on the silicon wafer will splash all over the place as the coating machine run at high speed, the splashed small particle then may pollute the film later on, when it dried out and forms small CDs film in the coating chamber.

The second factor is the running speed of the coater. The solution can also splash around when the coater runs at high speed, the speed should raise up gently, and then let

the film dry at high speed. Considering the splash of CDs solution, the base of coating machine must be covered with desiccant, which absorb the extra solution as the coating process was carried out.

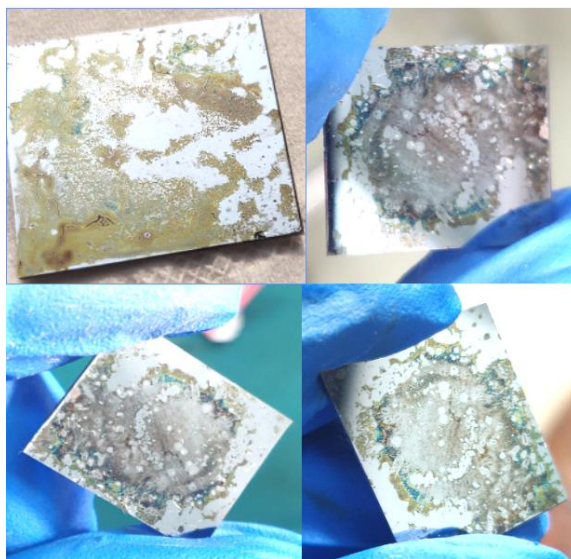


Figure 10. Failed CDs film.

The third factor is the solution itself. When the solution is too concentrated, the CDs particle just stacked on the silicon wafer, which forms the thick sticky brown substance. This kind of film can not tell any difference when putrescine vapor was blown onto it. So the solution should be as diluted as possible, and then do a large number of repeat spin coating. This way, a beautiful CDs film can be obtained in the end, but takes a lot of time.

Chapter 4 Conclusion

The synthesized CDs shows excellent dispersity as the TEM picture shows in the characterization process. But it's still not that easy to coat an uniform thin CDs film on a silicon wafer. So it's rather difficult to produce it with high efficiency. To get a beautiful CDs thin film, the CDs solution synthesized from the hydrothermal method must be diluted to a very thin solution with ultra-pure water. It also needs to repeat the coating process over and over again at the same time.

However, the sensing performance of the CDs film is satisfied. Although the film looks not very pleasant, it's very clear to observe the color change with naked-eyes. The sensing performance will certainly be improved as the film quality increases.

In all, this study provides a novel colorimetric detection method for organic amines, which based on the advanced carbon nanomaterial- carbon dots(CDs).

Bibliography

- [1] 赵中辉; 林洪; 王林; 等. 常见水产品中生物胺的调查及分析[J]. *水产科学* 2012, (31), 363-366.
- [2] Henao-Escobar, W.; del Torno-de Román, L.; Domínguez -Renedo, O *et al.* Dual enzymatic biosensor for simultaneous amperometric determination of histamine and putrescine[J]. *Food Chemistry* 2016, (190), 818-823.
- [3] Chi, H.; Liu, Y. J.; Wang, F *et al.* Highly Sensitive and Fast Response Colorimetric Humidity Sensors Based on Graphene Oxides Film[J]. *ACS Appl Mater Interfaces* 2015, (7), 19882-19886.
- [4] Kumar, Ravi; Kumar, Anil; Singh, Rakesh *et al.* Room temperature ammonia gas sensor using Meta Toluic acid functionalized graphene oxide[J]. *Materials Chemistry and Physics* 2020, (240), 121922.
- [5] Mkhoyan, K. Andre; Contryman, Alexander W.; Silcox, John *et al.* Atomic and Electronic Structure of Graphene-Oxide[J]. *Nano Letters* 2009, (9), 1058-1063.
- [6] Becerril, Héctor A.; Mao, Jie; Liu, Zunfeng *et al.* Evaluation of Solution-Processed Reduced Graphene Oxide Films as Transparent Conductors[J]. *ACS Nano* 2008, (2), 463-470.
- [7] Li, Feng; Yang, Dayong; Xu, Huaping. Non-Metal-Heteroatom-Doped Carbon Dots: Synthesis and Properties[J]. *Chemistry – A European Journal* 2019, (25), 1165-1176.
- [8] Shangguan, Jingfang; He, Dinggeng; He, Xiaoxiao *et al.* Label-Free Carbon-Dots-Based Ratiometric Fluorescence pH Nanoprobes for Intracellular pH Sensing[J]. *Analytical Chemistry* 2016, (88), 7837-7843.
- [9] Wang, Liang; Li, Ming; Li, Weitao *et al.* Rationally Designed Efficient Dual-Mode Colorimetric/Fluorescence Sensor Based on Carbon Dots for Detection of pH and Cu²⁺ Ions[J]. *ACS Sustainable Chemistry & Engineering* 2018, (6), 12668-12674.
- [10] Schoolaert, Ella; Hoogenboom, Richard; De Clerck, Karen. Colorimetric Nanofibers as Optical Sensors[J]. *Advanced Functional Materials* 2017, (27), 1702646.
- [11] Janzen, Michael C.; Ponder, Jennifer B.; Bailey, Daniel P *et al.* Colorimetric Sensor Arrays for Volatile Organic Compounds[J]. *Analytical Chemistry* 2006, (78), 3591-3600.
- [12] Liu, Bo; Sun, Hongjuan; Peng, Tongjiang *et al.* High selectivity humidity sensors of functionalized graphite oxide with more epoxy groups[J]. *Applied Surface Science* 2020, (503), 144312.
- [13] Park, H.; Lee, E.; Chung, Y *et al.* VOC Gas Sensors Fabricated with Graphene Oxide Composites for Food Safety and Quality[J]. *ECS Transactions* 2015, (69), 41-45.

- [14] Ahn, Hosang; Park, Jung-Hyun; Kim, Seon-Bae *et al.* Vertically Aligned ZnO Nanorod Sensor on Flexible Substrate for Ethanol Gas Monitoring[J]. *Electrochemical and Solid State Letters - Electrochem Solid State Lett* 2010, (13).
- [15] Paoprasert, Peerasak; Moonmuang, Hataipat; Supchocksoonthorn, Preeyanuch *et al.* *Materials Science and Engineering Conference Series* 2018, (378), 012003.
- [16] Khan, Syamantak; Verma, Navneet C.; Chethana *et al.* Carbon Dots for Single-Molecule Imaging of the Nucleolus[J]. *ACS Applied Nano Materials* 2018, (1), 483-487.
- [17] Wang, Li; Zhou, H. Susan. Green Synthesis of Luminescent Nitrogen-Doped Carbon Dots from Milk and Its Imaging Application[J]. *Analytical Chemistry* 2014, (86), 8902-8905.
- [18] Zhou, Yiqun; Mintz, Keenan J.; Sharma, Shiv K *et al.* Carbon Dots: Diverse Preparation, Application, and Perspective in Surface Chemistry[J]. *Langmuir* 2019, (35), 9115-9132.

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