

## Preparation and application of graphene and carbon quantum dot composites

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**Abstract:** Carbon quantum dots (CQDs) are mainly used to prepare novel functional carbon nanomaterials. Compared with traditional nano materials, carbon quantum dots have the advantages of good stability, light resistance, easy dispersion, low toxicity and environmental protection. Graphene is a new single-layer two-dimensional honeycomb structure, which is composed of  $sp^2$  hybrid carbon atoms. Graphene has excellent mechanical, optical and electrical properties. With the continuous progress of science and technology and the development of all walks of life, the research of single carbon materials has been difficult to meet the needs of development. The advantages of new carbon matrix composites are gradually emerging. Graphene doped composites were prepared by hydrothermal method, which can effectively improve the electrode performance. The results show that the doped graphene composite has good reversible capacity and cycle stability. Compared with single carbon materials, carbon quantum dots doped graphene composites can effectively improve their stability, electrical and optical properties.

**Keywords:** carbon quantum dots; graphene; microwave method; hydrothermal method

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### 1. Introduction

At present, carbon nanotube, carbon fiber and other basic materials, such as carbon nanotube and carbon fiber, have been found more and more in the form of carbon nanotube and graphite. Carbon nanomaterials are becoming more and more important.

Carbon quantum dots (CQDs) are carbon based zero dimensional materials. Carbon quantum dots have many advantages, such as excellent optical properties, low toxicity, good water solubility, wide sources of raw materials, environmental friendliness, low cost and good biocompatibility. The preparation of carbon quantum dots can be divided into two categories. The top-down methods are mainly ultrasonic method, hydrothermal synthesis method and electrochemical synthesis method. Graphene is a kind of new material with single-layer and two-dimensional honeycomb structure, which is composed of carbon atoms connected by  $sp^2$  hybrid. Graphene has excellent optical, electrical and mechanical properties. It has important application prospects in materials science, micro nano processing, energy, biomedicine and drug delivery, and is considered as a revolutionary material in the future<sup>[1]</sup>.

With the continuous development of carbon materials, with its unique excellent properties, it has been widely used in energy, capacitors, environment, high-tech industries and so on, and is developing in the direction of more and more environmental protection and humanization. Here are two new carbon materials, carbon quantum dots and graphene.

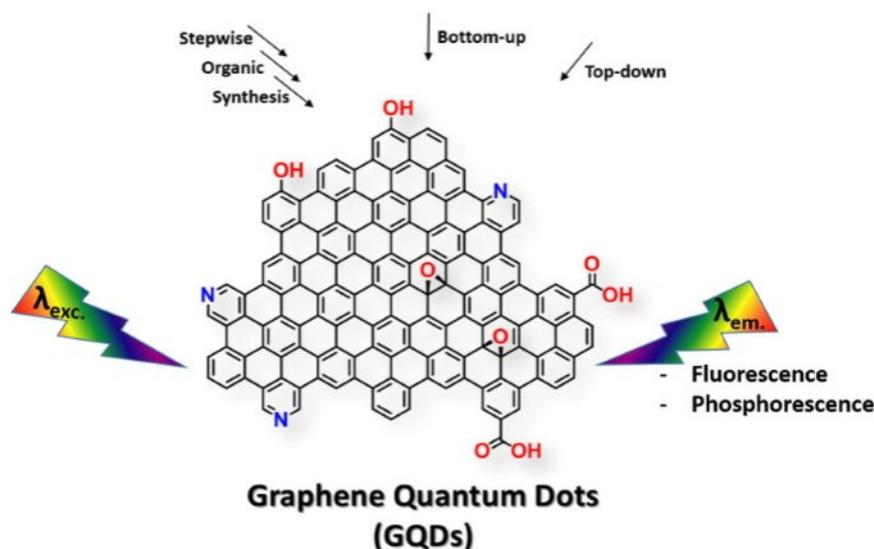


Fig. 1. Graphene structure diagram<sup>[20]</sup>

## 2. Experimental methods

### 2.1 Preparation of carbon quantum dots

In carbon nanomaterials, carbon quantum dots (CQDs) have attracted much attention due to their special fluorescence properties. When Xu et al. Prepared carbon nanotubes by arc discharge method for the first time, elemental analysis showed that the carbon content was 53.93%, nitrogen content was 1.20%, hydrogen content was 2.56%, oxygen content was 40.33%. In terms of definition, carbon quantum dots (CQDs) is a generalized concept, which can be summarized as carbon nanomaterials with diameter less than 10 nm suspended in solvent, referred to as carbon dots (CQDs). Carbon dots not only have fluorescence properties, but also show good biocompatibility, non-toxic, easy to modify and easy to functionalize. Based on their special size range, carbon dots have been widely used in optoelectronic devices, biological imaging, drug transport and other aspects<sup>[2]</sup>.

Since the birth of carbon quantum dots, a series of preparation methods have been developed. The following are two main methods to prepare carbon quantum dots<sup>[3]</sup>.

- (1) Arc discharge method: when Xu et al. Used electrophoresis to purify carbon nanotubes, a kind of fluorescent carbon point was occasionally obtained, which was a black suspension and kept uniform and stable for a long time. Dialysis

bags of different specifications were used for separation. When excited by 366 nm excitation light source, the molecular weight of carbon point is blue-green, yellow and orange. After that, Dawson et al. Dispersed carbon nanotubes in sodium dodecyl sulfate to obtain a green fluorescent carbon dot by ultrasonic, centrifugation and purification. The carbon quantum dots synthesized by this method have the characteristics of large oxygen content, small size and no surface modification.

- (2) Hydrothermal method: generally, organic solvent is used as reaction solvent, and selected organic compounds are added to prepare carbon quantum dots under high pressure and high temperature. In 2010, Zhang et al reported for the first time the preparation of carbon dots by one-step hydrothermal method. In this method, ascorbic acid was used as carbon source, water and ethanol as solvent, and the quantum yield was only 6%. Although the hydrothermal method is slightly complicated in the post-treatment reaction liquid, due to its simple operation and controllable experimental conditions, there are many similar reports. There are fluorescent carbon quantum dots prepared by hydrothermal method using sugar, orange juice and silk as carbon sources respectively, but these yields are not very high.
- (3) Electrochemical oxidation: In 2007, the electrochemical oxidation of carbon nanotubes from carbon nanotubes was about 6.4% by using the electrochemical method. In 2012, Ming et al. Successfully achieved large-scale preparation of carbon quantum dots using pure water as electrolyte, and further simplified the subsequent processing steps. Therefore, electrochemical oxidation method for preparing carbon dots has been accepted by more and more research groups.



Fig. 2.1. Variation diagram of the reaction process of carbon quantum dots prepared by electrochemical

- (4) Microwave method: In 2009, Zhu et al. Prepared carbon dots with different luminescence wavelengths from glucose and PEG 2000 by microwave heating and later separation, with quantum yield of 3.1%. In 2011, Liu et al. Prepared blue light carbon quantum dots using glycerol and phosphate under microwave heating conditions. The microwave method has the advantages of simple preparation conditions, controllable preparation time and simple carbon source.

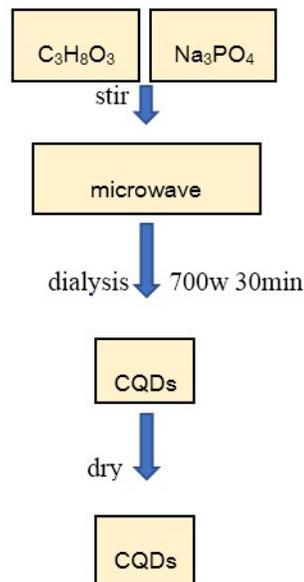


Fig. 2.2. Schematic diagram of carbon point preparation by microwave

## 2.2 Preparation of graphene

Since 2004, graphene has been mechanically stripped of graphene by physicist Andre Geim and others to obtain single-layer graphene. Graphene has been explored by more and more researchers. Structurally, graphene is a single-layer carbon atom structure formed periodically in two-dimensional plane with a benzene six membered ring as its basic structural unit. The theoretical thickness is only one carbon atom diameter, about 0.335 nm. The two carbon atoms in each cell of graphene are determined by lattice vectors  $a_1$  and  $a_2$ . The carbon atoms are hybridized into bonds by  $sp^2$ , and the bond length is 0.142 nm. The  $sp^2$  orbital of each carbon atom is hybridized with three adjacent carbon atoms to form  $\sigma$  bond, and the remaining p orbital overlaps with each other to form  $\pi$ - $\pi$  conjugate system. Due to the thermodynamic instability of single-layer graphene, there are many problems such as surface wrinkles, holes and uneven thickness<sup>[4]</sup>.

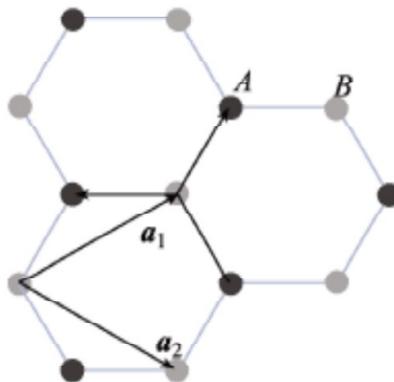


Fig. 2.3. Two-dimensional crystal structure of graphene

The preparation methods of graphene can be divided into physical method and chemical method. The physical method includes mechanical stripping method, gas phase stripping method and orientation attachment method. Chemical methods include: redox method, chemical vapor deposition method, crystal epitaxial growth method and so on<sup>[5]</sup>.

- (1) Mechanical stripping method: Mechanical stripping is a method to obtain graphene thin layer material by friction and relative motion between object and graphene. Using 1 mm thick graphite sheet as raw material, the graphite sheet surface was etched by plasma to make it adhere to the glass substrate. Then, 1 μm thick tape was used for continuous stripping. Finally, the exfoliated sample was dispersed with acetone solution, and then dried and cleaned to obtain single-layer graphene. Using carbon as raw material and solid particles as working medium, a large amount of graphene can be prepared by ball milling with high yield.
- (2) Gas phase stripping method: The volume of graphite can be increased by converting solid phase into gas phase directly, which can effectively separate graphite into graphene. Using expanded graphite as raw material and dispersing in ammonia water, graphene sheet can be stripped by gas phase stripping method. Graphene aqueous solution can be prepared by immersing graphite in supercritical CO<sub>2</sub> and adding gas to sodium dodecyl sulfonate for washing.
- (3) Vapor deposition (CVD): The gas deposition method was used to prepare graphene films. Carbon containing gas was used as the raw material, which was continuously passed into the copper and nickel metal catalyst substrate containing carbon content, and the carbon atoms generated by gas molecules were thermally decomposed under high temperature conditions, and then these decomposed carbon atoms were continuously deposited on the substrate, and finally graphene materials were prepared<sup>[6]</sup>.
- (4) Oxidation-reduction: GO can be prepared by oxidizing natural graphite with sulfuric acid, potassium permanganate and hydrogen peroxide, which can increase the distance between graphite layers and insert oxides between graphite layers. Graphene oxide can also be prepared by high temperature expansion method and physical stripping method. Finally, reduced graphene oxide (rGO) was obtained by chemical reduction.

### **2.3 Graphene and carbon quantum dot composites**

Because Gr has no band gap, its conductivity can not be well controlled, and the surface of Gr is smooth and inert, which is not conducive to composite with other materials, thus hindering the application of Gr<sup>[7]</sup>. Doping is a good method to improve the properties of carbon materials. The preparation methods of carbon quantum dots are widely used because of their wide sources and low cost. The results show that the doped graphene (GO@CQDs) has been widely used in the field of lithium-ion fuel cell. At present, the doping of carbon quantum dots in graphene has become a research hotspot<sup>[8-10]</sup>.

### 3. Experimental process

#### 3.1 Preparation of carbon quantum dots

Microwave method is to obtain carbon quantum dots by heating carbon precursor. In this paper, glycerol is used as raw material<sup>[11]</sup>. Of course, microwave method also has some advantages, such as the simple preparation process, the heating temperature can be adjusted, and the time-consuming is short. It is also an excellent rapid preparation scheme of carbon quantum dots<sup>[16-17]</sup>. It is an excellent scheme for rapid preparation of carbon quantum dots.

Prepare 7.1 mmol 0.5668 g  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ , put the weighed  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  into a 500 ml beaker, mix with 210 ml deionized water, and stir evenly to obtain  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  aqueous solution. Then take seven 500 ml measuring cylinders, divide 490 ml glycerol into seven measuring cylinders, and add trisodium phosphate equally into the seven beakers, so that each beaker contains 70 ml glycerol and 30 ml trisodium phosphate aqueous solution and mixed solution. Set the microwave time 25-45 min, microwave power 700 w, start the experiment and record the data.

Start the test: the solutions in 7 beakers were treated according to different test conditions, and the control group was set up. The processing is as follows:

Table 1 Experimental data table

Condition Number	Power (w)	Time (min)	PEG (drops)
1	700	25	0
2	700	25	2
3	700	25	4
4	700	35	0
5	700	35	2
6	700	35	4
7	700	35	6
8	700	45	0
9	700	45	2
10	700	45	4

#### 3.2 Preparation of GO@CQDs by hydrothermal method

Carbon point was prepared by microwave method with microwave power of 700 w and heating time of 30 min respectively. The carbon point reaction solution was prepared by dialysis and drying<sup>[18-20]</sup>. Then 100 ml of carbon quantum dots prepared by different

microwave time and 100 ml graphene aqueous solution (1.0 g GO dispersed in 1000 ml deionized water) were measured respectively. After ultrasonic treatment for 3 h, magnetic stirring was conducted for 2 h, and ultrasonic wave was conducted for 3 h. Centrifuge was used to rotate at 3000 r/min for 4 h. The supernatant was centrifuged at 0-5 ! for preparation, mixed evenly, added to PTFE liner, put into high-pressure reactor, heated at 150 ! for 2 h. Finally, the original solution prepared by hydrothermal method is dialyzed and dried, and the sample is ready for use. That is to say GO@CQDs compound<sup>[13-15]</sup>.

#### 4. Results and discussion

The morphology and properties of the composite were analyzed by instrument. The morphology of the composite was characterized by SEM and TEM. The structure and structure of the composite were characterized by IR, UV, Raman and XRD<sup>[12]</sup>.

##### 4.1 Ultraviolet absorption spectrum analysis of carbon quantum dots

After the experiment, the products were separated by centrifugation, and the solutions 'a' and 'b' were prepared by adding deionized water into experimental groups 1, 2 and 3 according to the ratio of products: Deionized water = 1:9 And 2:8; the solutions of experimental groups 4, 5, 6 and 7 were added with deionized water according to the ratio of products: Deionized water = 1:9 And 2:8; the solutions of experimental groups 8, 9 and 10 were added and separated according to the ratio of products: Deionized water = 2:8, the sub water is prepared with solutions (8, 9, 10). The UV absorption spectrum was obtained by characterizing each group with UV absorption spectrum. The data of the obtained spectrogram were mapped with origin and analyzed as follows:

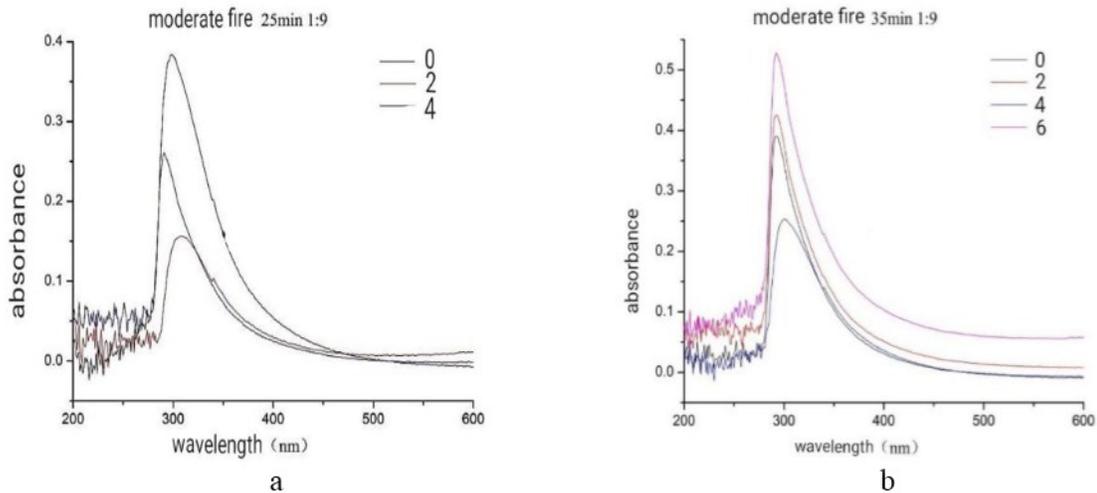


Fig. 4.1. a: medium fire 25 minutes; b: medium fire 35 minutes

It can be seen from Fig. 4.1a that the absorption band of the spectrum is between 250 nm and 350 nm. It can be seen from the figure that the position of the maximum

peak is at 295 nm wavelength. The corresponding absorbance of 'c' is 0.38, that of 'a' is 0.15, and that of 'b' is 0.25. In addition, it can be seen that after the peak value, the absorbance decreases slowly with the increase of wavelength, among which 'c' decreases fastest, and the absorbance decreases slowly, and finally tends to be stable. It can be seen from figure b that the absorption band of the spectrum is between 250 nm and 350 nm. It can be seen from the figure that the position of the maximum peak is at the wavelength of 295 nm. The corresponding absorbance of 'c' is 0.38, that of 'd' is 0.42, that of 'e' is 0.25, and that of 'f' is 0.53. In addition, it can be seen that the absorbance decreases slowly with the increase of wavelength after the peak value, and the absorbance decreases slowly and finally tends to be stable.

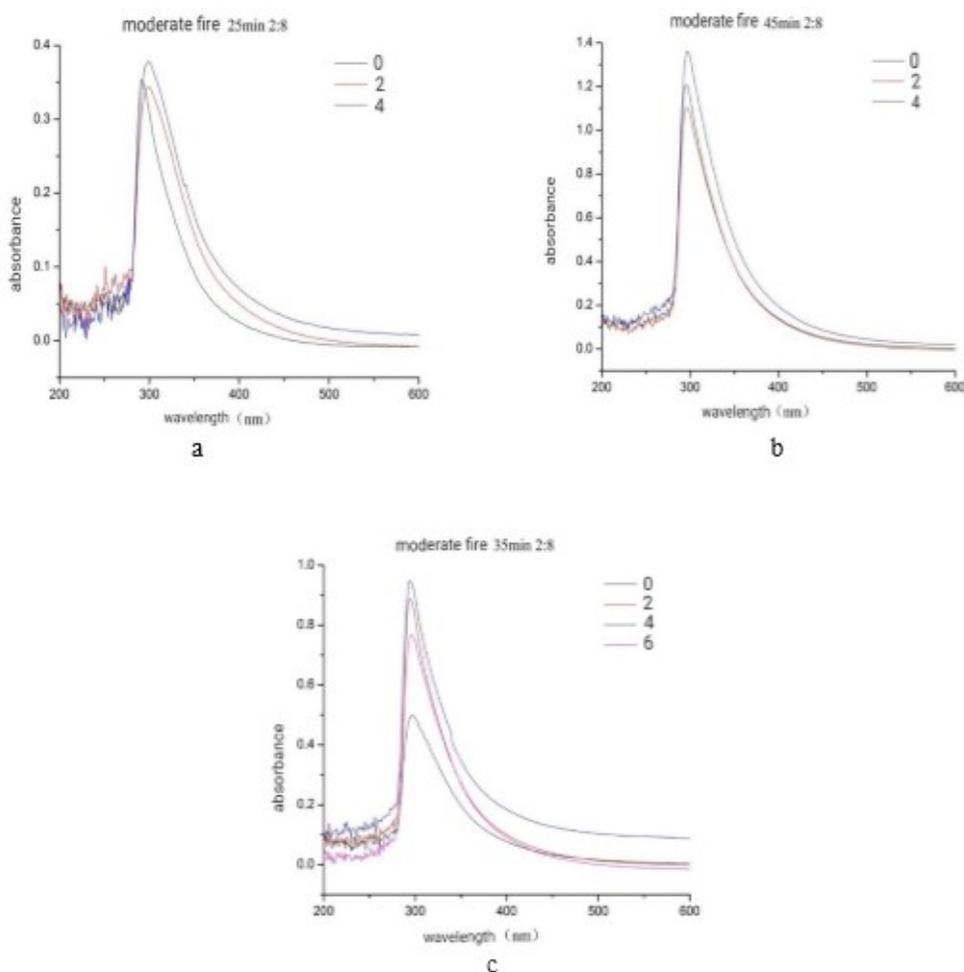


Fig. 4.2. a: medium fire 25 minutes; b: medium fire 35 minutes; c: medium fire 45 minutes

It can be seen from Fig. 4.2a that the absorption band of the spectrum is between 250 nm and 350 nm. It can be seen from the figure that the position of the maximum peak is at the wavelength of 295 nm. The corresponding absorbance of 'c' is 0.38, that of

d\$ is 0.42, that of e\$ is 0.25, and that of f\$ is 0.53. In addition, it can be seen that the absorbance decreases slowly with the increase of wavelength after the peak value, and the absorbance decreases slowly and finally tends to be stable. It can be seen from b that the absorption band of the spectrum is between 250 nm and 350 nm. It can be seen from the figure that the position of the maximum peak is at 295 nm wavelength. The corresponding absorbance of ' \$ is 0.35, that of a\$ is 0.34, and that of b\$ is 0.38. In addition, it can be seen that after the peak value, the absorbance decreases slowly with the increase of wavelength, among which ' \$ decreases fastest, and the absorbance decreases slowly, and finally tends to be stable. It can be seen from c that the absorption band of the spectrum is between 250 nm and 350 nm. It can be seen from the figure that the position of the maximum peak is at the wavelength of 295 nm. The corresponding absorbance of c\$ is 0.49, that of d\$ is 0.84, that of e\$ is 0.87, and that of f\$ is 0.68. In addition, it can be seen that the absorbance decreases slowly with the increase of wavelength after the peak value, and the absorbance decreases slowly and finally tends to be stable.

#### 4.2 Morphology analysis

As shown in Fig. 4.3, Fig. a is the SEM photo of GO. It can be seen from the figure that the surface folds of graphene oxide are obvious and rough, and there are a lot of interlayer accumulation. Fig. b is a picture of the GO@CQDs material, in which the curliness of graphene increases, indicating that the carbon point doping not only maintains the original structure of graphene, but also improves the mechanical strength and specific surface area of graphene.

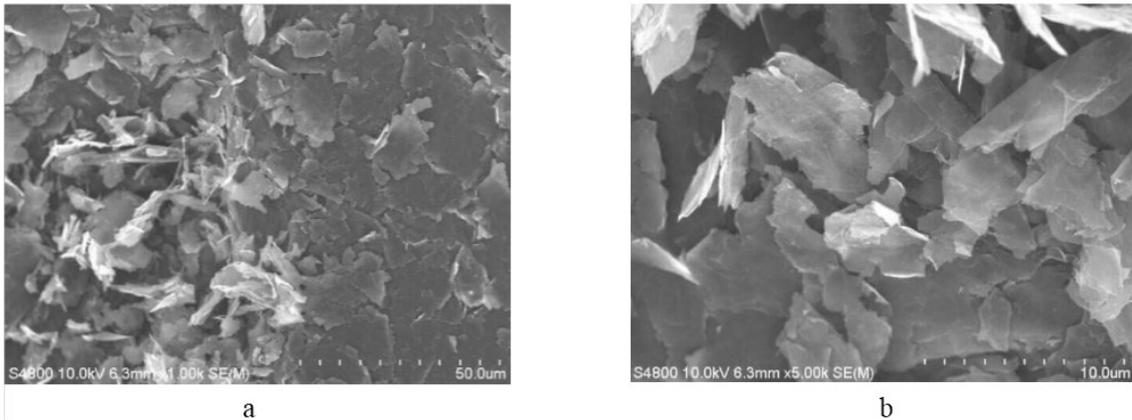


Fig. 4.3. a: SEM of GO; b: SEM of GO@CQDs

#### 4.3 Analysis of GO and GO@CQDs with XRD

Fig. 4.4 shows GO and GO@CQDs. It can be seen that the XRD patterns of the two materials are basically similar, indicating that the doping of carbon point does not affect the crystal structure of graphene.

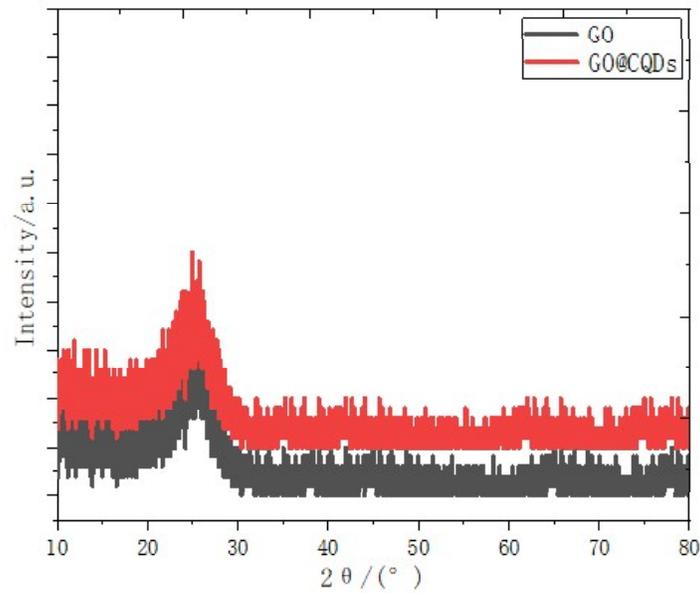


Fig. 4.4. XRD of GO and GO@CQDs

#### 4.4 Ultraviolet absorption spectrum

As shown in Fig. 4.5, which is the UV absorption spectrum of GO and GO@CQDs. There is a strong absorption peak at 220-240 nm, which may be caused by the transition of N- $\delta$  bond of carbon atom, which may be caused by the formation of C-C single bond by the reaction of C=C double bond in graphene structure during the recombination process of Gr and CQDs, and the length of conjugated system decreases.

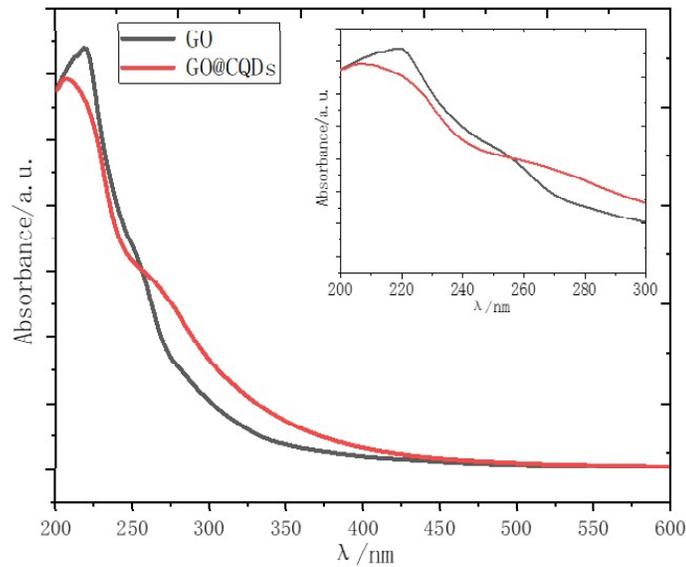


Fig. 4.5. Ultraviolet absorption spectra of GO and GO@CQDs

#### 4.5 Infrared spectrum

Figure 4.6 shows the infrared spectra of GO and GO@CQDs. It can be seen from the figure that  $500\text{--}600\text{ cm}^{-1}$  is the stretching vibration of C-Br,  $1610\text{ cm}^{-1}$  is the asymmetric stretching vibration of C-O bond,  $1740\text{ cm}^{-1}$  is the stretching vibration of C=C bond on benzene ring,  $2920\text{ cm}^{-1}$  is the stretching vibration of C-H bond, and the stretching vibration of -OH at  $3425\text{ cm}^{-1}$  is the hydroxyl group formed by hydrogen bonding of carbon point and graphene oxide. It can be concluded that there are a large number of hydrogen and oxygen functional groups on the surface of graphene doped with carbon quantum dots, which improves its properties.

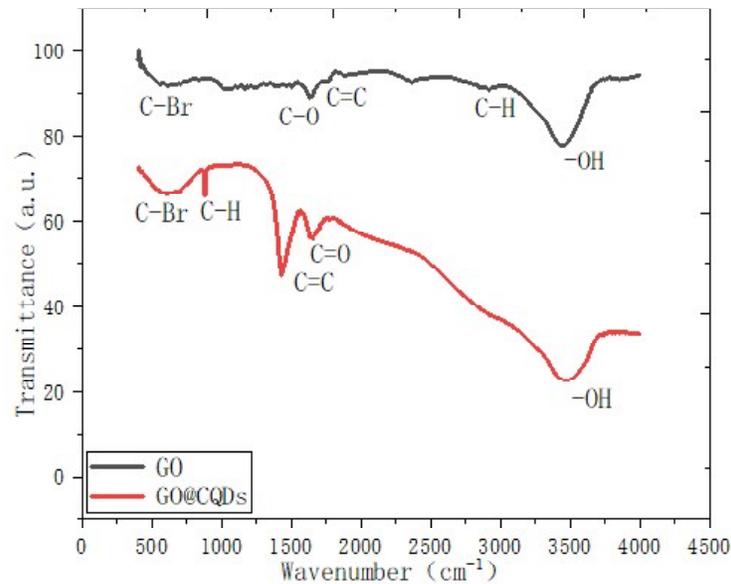


Fig. 4.6. Infrared spectra of GO and GO@CQDs

#### 4.6 Conclusion of this chapter

In this paper, the preparation technology of carbon point composites was studied, using microwave method and electrochemical oxidation method respectively. Then graphene matrix was introduced and modified with carbon dots GO@CQDs Materials, study its performance advantages.

The surface of carbon dots prepared by microwave method contains abundant hydrogen and oxygen functional groups, which were successfully prepared by hydrothermal method and graphene oxide GO@CQDs Materials and carbon dots greatly improve the lamellar structure of graphene, effectively alleviate the stacking fold phenomenon, enhance the mechanical strength of graphene, and increase the effective specific surface area of graphene. At the same time GO@CQDs contains abundant functional groups and more active sites.

## 5. Conclusion

In this paper, the preparation technology of new carbon nanoparticles carbon dots was explored, mainly by microwave method. The carbon dots prepared by microwave method were used as electrode materials, and the electrochemical performance was improved after the carbon dots were compounded. Then graphene matrix was introduced and modified with carbon dots GO@CQDs Material Science.

In the microwave method, glycerol was used as carbon source to prepare carbon dots in trisodium phosphate aqueous solution by microwave. At the same time, glycerol passivated the carbon dots, which made the carbon dots have good fluorescence and water solubility. Carbon dots were prepared from graphite rods by electrochemical oxidation. In contrast, the carbon dots prepared by microwave method contain more hydrogen and oxygen functional groups, and the preparation process conditions are simple and controllable. The morphology and size of carbon dots can be effectively adjusted. At the same time, the preparation time is short, which can be used for large-scale preparation, and has a better application prospect.

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