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IMPROVED SOLVOTHERMAL METHOD FOR CUTTING GRAPHENE OXIDE INTO GRAPHENE QUANTUM DOTS

L. M. DONG[a,b,*], D. Y. SHI[a], Z. WU[a], Q. LI[a], Z. D. HAN[a,b]
[a]*College of Materials Science and Engineering, Harbin University of Science and Technology, Harbin, China*
[b]*Key Laboratory of Engineering Dielectrics and Its Application, Ministry of Education, Harbin University of Science and Technology, Harbin, China*

An improved method for the preparation of graphene quantum dots (GQDs) is described. The samples are characterized in terms of morphological, structural, and optical properties which are evaluated by X-ray diffraction (XRD), transmission electron microscopy (TEM), the Photoluminescence (PL) spectrum and Fourier transform infrared (FTIR) spectra correspondingly. The graphene oxide (GO) go through with microwave expansion treatment first, then followed by solvothermal process. The research shows that with the increase of the microwave time and microwave power, the fluorescence intensity of GQDs first increased and then decreased, when the GO sheets are under 500 W microwave-assisted treatment for 5 min, the intensity gets the strongest. The solvothermal temperature had no effect on the fluorescence emission wavelength of the graphene quantum dots, the fluorescence emission spectra red shifts as the microwave treatment time is increased. The fluorescence emission spectrum of GQDs that synthesized by this method perform excitation-dependent PL behaviors.

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1. Introduction

In recent years, with the study of graphene materials continue to rise, graphene quantum dots (GQDs) because of the minisize approximate zero dimensional apparent quantum confinement[1,2] and edge effects[3] has more attractive application prospect in many areas such as solar photovoltaic devices, biological medicine, light-emitting diodes and sensor, GQDs show considerably low toxicity, high stability[4], high electrical conductivity and high thermal conductivity. In particular, recent advances have been made in the solution synthesis of colloidal GQDs[5], which provides a solution platform to investigate their optical and optoelectronic properties as well as novel applications, graphene quantum dots (GQDs) have attracted great attention for their unique properties[6,7]. Because of their great scientific and technological interests, it is of importance to develop their size- and shape-controlled synthetic methods, including top-down[8,9,10]and bottom-up strategies[11,12]. The main methods for preparing graphene quantum dots include hydrothermal graphene oxide reduction[13,14,15]electrochemical[16] and

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[*] Corresponding author: donglimin@hrbust.edu.cn

metal-catalyzed[17]approaches, chemical synthesis[18,19] chemicalexfoliation[20], electron beam lithography[21], and pulsed laser synthesis. Recent years, a microwave pyrolysis method has been developed to prepare carbon nanoparticles[22,23] with particle size ranging from 1 to 5 nm.

Microwave-assisted technique has been widely applied to materials synthesis. The GQDs were prepared by a micro-wave-assisted hydrothermal method that combined both the advantages of hydrothermal and microwave techniques[24]. The microwave heating provides rapid, simultaneous, and homogeneous heating, leading to uniform size distribution of quantum dots，and thus reaction time is dramatically shortened, product yields and purities was greatly improved[25]. Tang et al. reported a microwave-assisted hydrothermal method that combined both the advantages of hydrothermal and microwave techniques to pyrolyze the glucose. On the basis of the versatility of microwave, it is potentially promising to explore the rapid one-step synthesis of luminescent GQDs. And it is indicated that GQDs can emit a strong green fluorescence, and have low toxicity, good water solubility, fluorescent stability and bio-compatibility. Graphene quantum dots can be used for biological probe, biomarkers.

Herein, we report a facile microwave assisted solvothermal approach for the preparation of stabilizer-free blue-green-luminescent GQDs from GO nanosheets. The graphene oxide (GO) go through with microwave pretreatment first, and then the solvothermal reaction is under way in different temperature.

2. Materials and Methods

2.1. Materials Preparation

The GO nanosheets were synthesized by modified Hummers method. It was heated by a conventional microwave oven at a certain power (300, 500, 800 and 1000 W) for a period of time (1, 3, 5, 7 and 9 min) to complete the pre-processing of precursor. After cooling to room temperature, the sample was dissolved by N, N dimethylformamide (DMF) . After ultrasonic treatment for two hours, the mixture was transferred into polytetrafluoroethylene autoclave and heated in different temperatures for 8 h. The experimental parameters have a distinct effect on the growth of GQDs such as microwave power, heating time, source concentration, etc.

2.2. Analysis Methods

TEM measurements were performed on JEOL, JEM-2010F at operating voltage of 200 kV. The Fourier transform infrared (FTIR) spectra of the samples were obtained using the KBr pellet method by Thermo Nicolet Avatar 360 spectrometer with a resolution of 4 cm^{-1}. For PL characterizations, the excitation and emission spectra of the GQDs solutions were recorded by Shimadzu RF-5301PC Analytical Instrument apparatus with Xe lamp as excitation source.

3. Result and Discussion

3.1. Morphology analysis

Unstable oxygen-containing functional groups in the middle and the edge of the GO sheets were decomposed to carbon dioxide under the microwave treatment, so the pressure generated between the GO layers. When the pressure is higher than the layers' van der Waals force, the GO sheets were exfoliated to thinner slices. Fig. 1 is the transmission electron microscopy (TEM) images of the synthesized GQDs. Fig. 1(a) and (b) are the GO before and after microwave treatment, respectively. We can see that after microwave treatment, the thickness of the GO sheet became thinner, which leads to wrinkle. The GQDs were prepared by the microwave assisted solvothermal approach from GO nanosheets. The morphology of GQDs are shown in Fig. 1 (c) and (d). We can see that the diameters of GQDs is mainly distributed in the range of 5 ~8 nm.

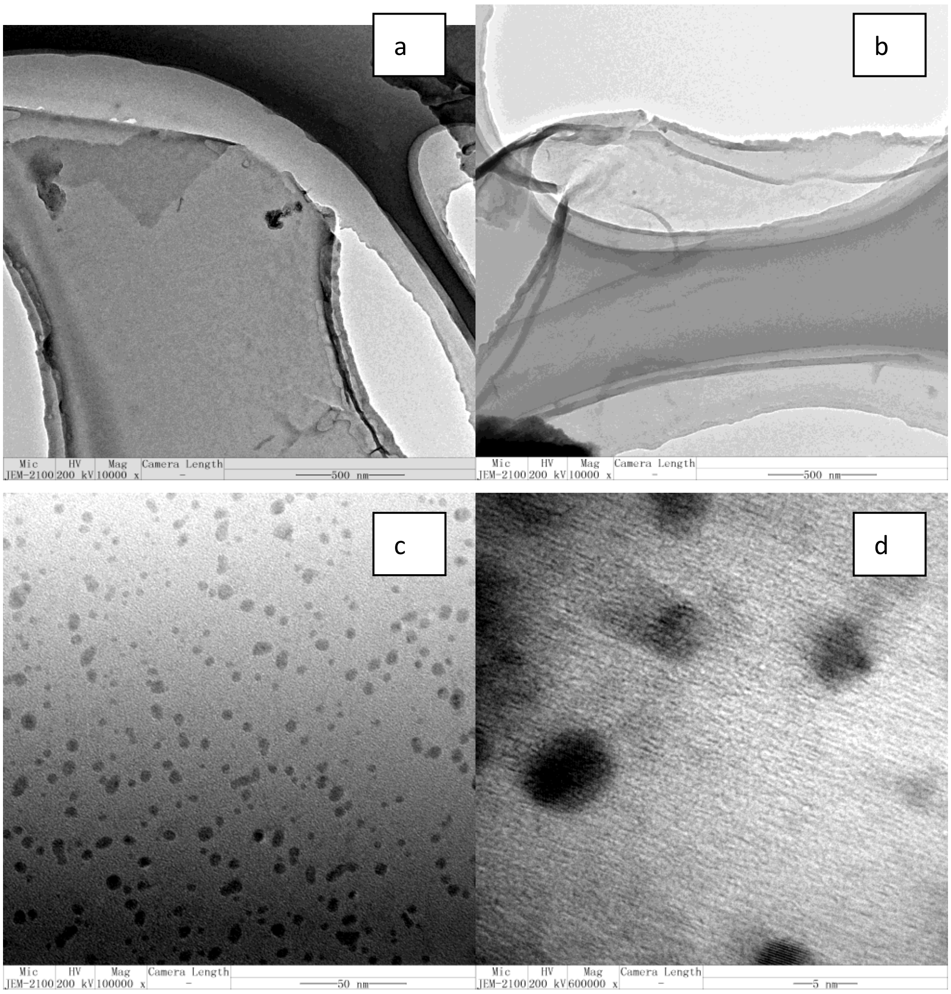

Fig. 1 TEM of a) GO before microwave treatment, b) GO after microwave treatment, c) and d) are GQDs

3.2 Crystal structure analysis

X ray diffraction was used to determin the crystal structure of GQDs. As shown in Fig. 2, diffraction peak of GO (001) crystal face is located at 12.7 °, that's a strong and sharp peak, while the diffraction peak of GQDs (001) crystal face located at 7.3 °. According to Bragg formula:

$$2d\sin\theta = n\lambda \tag{1}$$

GQDs interlamellar spacing: d = 12.11 Å. Meanwhile, diffraction peak of (002) crystal face is at 23°, the peak shape looks like bread peak, and the peak is not obvious.

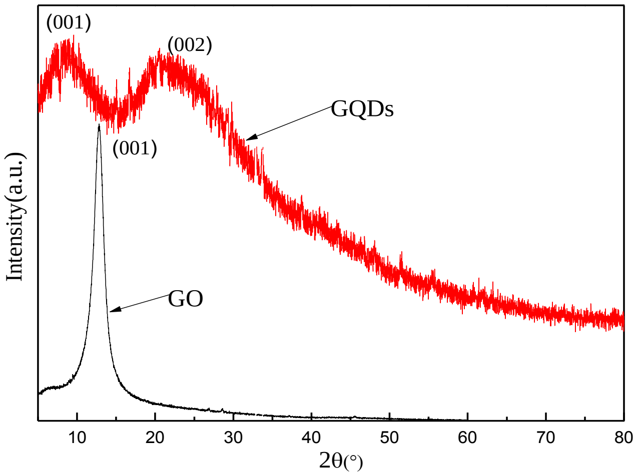

Fig.2 XRD of GO and GQDs

3.3. Functional group analysis

Fig. 3 is the FTIR spectrum of GO and GQDs. After microwave and solvothermal treatment, the in-plane and out-plane bending vibration peak of -OH are at 1382 cm^{-1}, 700 cm^{-1}, respectively. Stretching vibration peak of C-H appeared at 2927 cm^{-1}. At the same time, the stretching vibration peak of C-O-C at 1089 cm^{-1} disappeared, which indicates that the bridge oxygen atoms were removed in the reaction. The new fracture is connected with another kind of oxygen containing function groups such as –OH. After the process of micro-wave-assisted hydrothermal method, smaller sized GQDs were obtained, and the prepared GQDs have a good hydrophilic property .

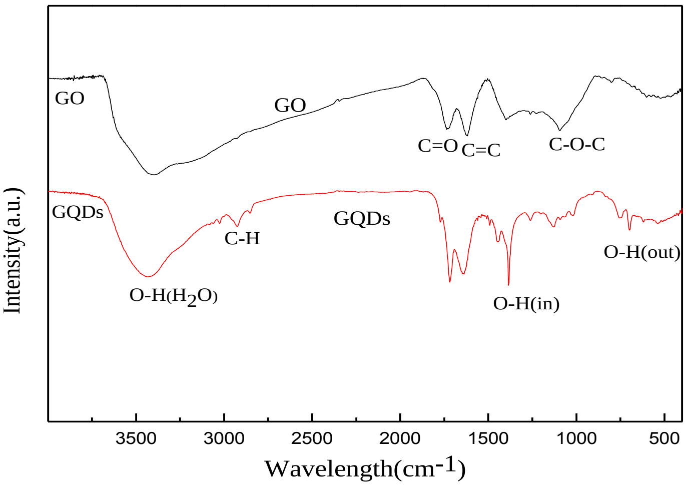

Fig. 3 FTIR spectrum of GO and GQDs

3.4. Fluorescence analysis

Spectral analysis was carried out on the GQDs. As shown in Figure 4, GQDs have strong absorption in ultraviolet band, but it has no obvious characteristic absorption peak, which fits with the semiconductor nanomaterials ultraviolet absorption spectrum. In addition, a shoulder peak at 276 nm indicates the existence of functional groups with lone pair electrons (such as carboxyl etc.).

GQDs have broad excitation peak and narrow emission peak. The PL excitation (PLE) spectrum shows two sharp peaks at 381 and 413 nm. And the two excitation all induce the strongest PL at 486nm. When the excitation wavelength is changed from 420 to 500 nm, the PL peak shifts from 498 to 544 nm, luminous intensity followed by decline. The emission wavelength of GQDs changes with the variation of the excitation wavelength. GQDs exhibit an excitation-dependent PL behaviors, which is same with the carbon quantum dots.

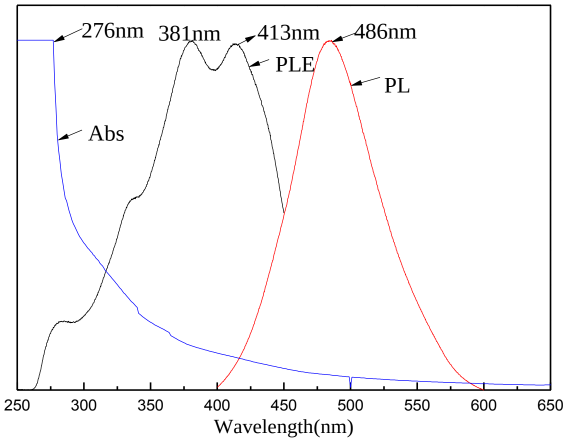

Fig.4 Normalization of UV-vis absorption and fluorescence spectra of GQDs

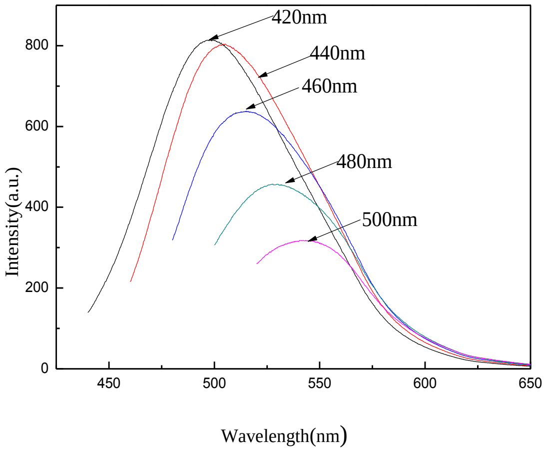

Fig.5 PL spectra of the GQDs at different excitation wavelengths

3.5. Influence of experimental conditions on the fluorescence properties of GQDs

3.5.1 Effect of the microwave power

Fig.6 shows the XRD patterns of RGO and GQDs under different microwave power in the microwave. We can learn that with the increase of microwave power, the (002) diffraction peak of GQDs is close to the (002) diffraction peak of graphene, and the crystal structure of the GQDs is close to the crystal structure of the graphene too. When the power is up to 800 W, the crystal structure of GQDs is close to the crystal structure of graphene. When the power continues to increase, (002) diffraction peak appears left shift. The reason for this phenomenon may be that the graphene oxide was further carbonized because of the excessive microwave power.

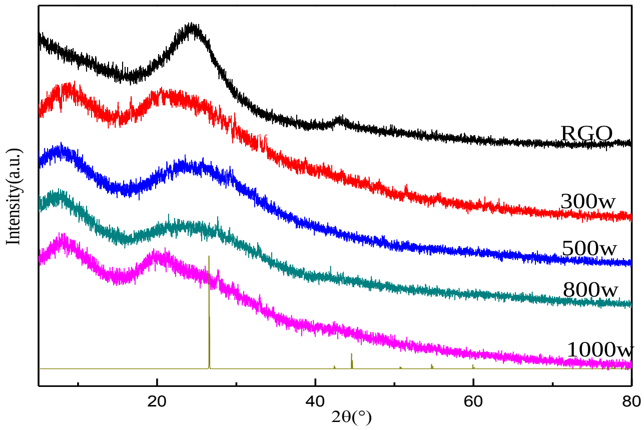

Fig.6 XRD patterns of RGO and GQDs which under different microwave power

Fig.7 is the FTIR spectrum of GO and GQDs which are under different microwave powers. With the microwave power increased, the intensity of C-O-C stretching vibration peak at 1089 cm^{-1} is becoming increasingly weak, when the power is up to 1000 W, the C-O-C stretching vibration peak disappears. Meanwhile the intensity of out- plane bending vibration peak of -OH at 700 cm^{-1} is also reduced. Therefore, we analyze that reduction reaction of the partial graphene oxide have been occured during the pre-microwave treatment, oxygen-containing groups were destroyed and the bridge oxygen atoms were removed.

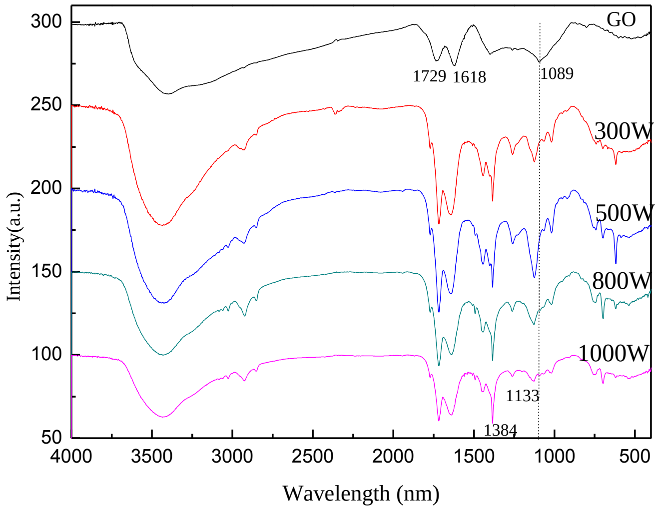

Fig.7 FTIR spectrum of GO and GQDs which under different microwave power

Microwave power has a significant effect on the fluorescence properties of GQDs (Fig. 8). The microwave time is set to 3 min, and the GO sheets are carried out under different microwave power. With the increase of the microwave power, the fluorescence intensity of GQDs first increased and then decreased, when the microwave power was set to 500 W, the intensity got the strongest. With the increase of microwave power, interlamellar spacing of GO is constantly increasing. In the process of reaction, bridging oxygen atoms have been removed, that promoted the fracture of the oxygen-containing groups. We can get smaller size quantum dots, it can also improve the quantum yield, fluorescence intensity then increased. But when the microwave power continues to increase, a portion of GO was carbonized, and the fluorescence intensity decreased.

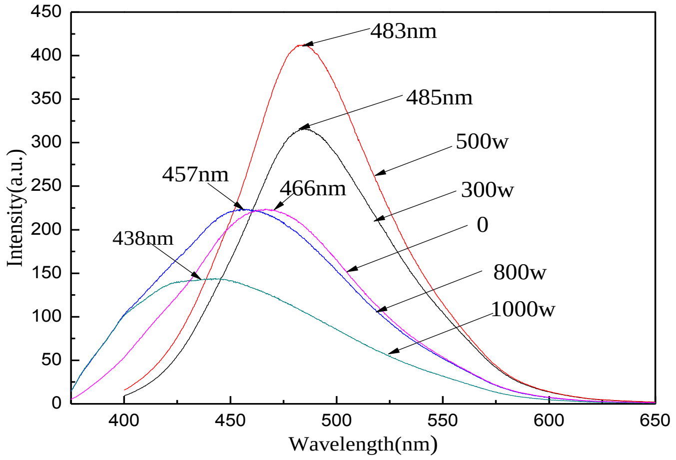

Fig.8 PL spectra of the GQDs which under different microwave power

3.5.2 Effect of the microwave time

Fig.9 is the XRD patterns of RGO and GQDs that are under different microwave time. We can see that (001) crystal plane diffraction peak of graphene quantum dots is about 7.8°. According to Bragg formula (1), GQDs interlamellar spacing: d = 11.33Å. (002) crystal surface appears at approximately 24°, it was the characteristic diffraction peaks of graphene. With the increase of microwave time, the diffraction peak of GQDs is close to the standard diffraction peak of graphene (26°), and the crystal structure of the GQDs is close to the crystal structure of the graphene as well. The microwave power is set to 800 W power here.

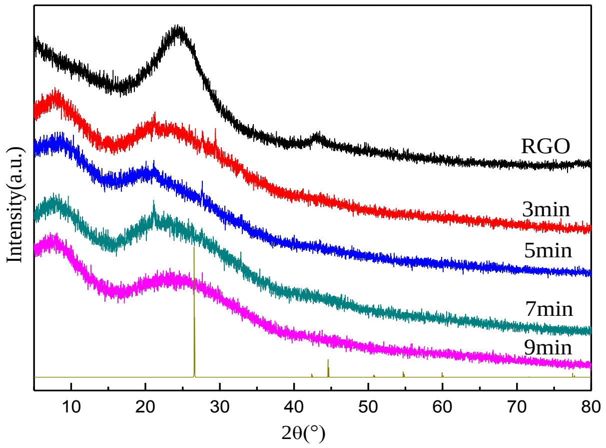

Fig.9 XRD patterns of RGO and GQDs that under different microwave time

From the Fig.10 we can learn that the in-plane and out-plane bending vibration peak of -OH are at 1382 cm^{-1}, 700 cm^{-1}, respectively. Phenolic hydroxyl stretching vibration peak appears at 1133cm^{-1}, -COOH and C = C stretching vibration peak (1729 cm^{-1} and 1618 cm^{-1})still exists.

With the increase of microwave time, the intensity of the phenolic hydroxyl stretching vibration peak (1133 cm^{-1}), the carboxyl and the C = C stretching vibration peak (1729 cm^{-1},1618 cm^{-1})increased gradually . When the microwave time is up to 5 min, the -COOH and C=C stretching vibration peak are the weakest, and the C-O-C stretching vibration peak at 1089 cm^{-1} disappeared. The reason for this phenomenon is that the GO sheets were further exfoliated under the influence of microwave, so the number of layers of prepared quantum dots become less. GO was further oxidized at air atmosphere under the continuous microwave, oxygen-containing groups were added between the GO sheets, this promote the stripping of the graphene oxide sheets, and the amount of oxygen-containing groups increased.

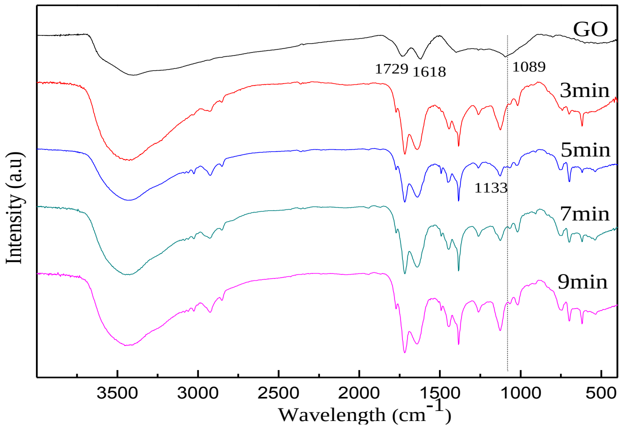

Fig.10 FTIR spectrum of GQDs that under different microwave time and GO

Microwave time also has a significant effect on the fluorescence properties of GQDs. GO sheets are under microwave power of 500 W for different times. Fig.11 is the emission spectrum of samples. With the increase of the microwave time, the fluorescence intensity of GQDs first increased and then decreased, when the microwave time was set to 5 min, the intensity got the strongest. The appropriate microwave power and time can improve the fluorescence properties of GQDs. Besides, it can also improve the quantum yield, so the fluorescence intensity of GQDs increased. But the high concentration of GQDs in the solution lead to concentration quenching effect, the fluorescence intensity decreased instead.

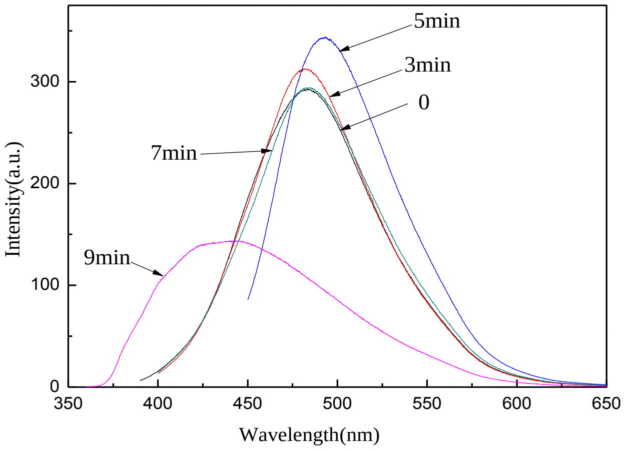

Fig.11 PL spectra of the GQDs which under different microwave time

3.5.3 The effect of the Solvothermal temperature on the GQDs

Fig.12 shows the fluorescence emission spectra of GQDs at the different solvothermal temperature (160 °C，170 °C，180 °C，190 °C). Temperature has no effect on the fluorescence emission wavelength of the graphene quantum dot. With the increase of the solvothermal temperature, the fluorescence intensity of GQDs first increased and then decreased. The yield of graphene quantum dots is on the increase when the temperature increases. But when the temperature continues to increase, a portion of GO was carbonized, and then the fluorescence intensity decreased.

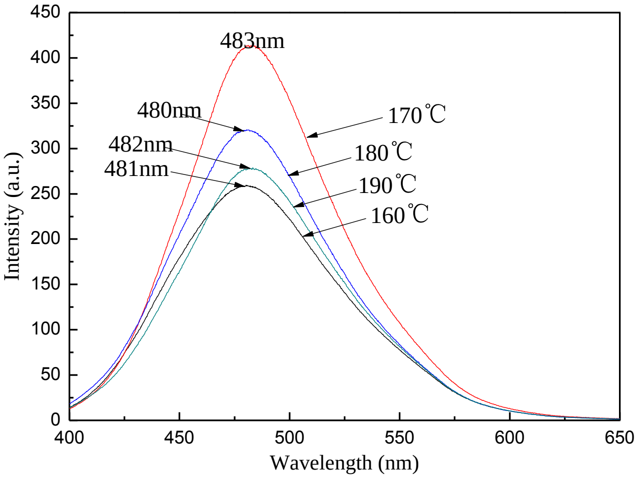

Fig. 12 The fluorescence emission spectra of GQDs at the different Solvothermal temperature

4. Conclusion

Highly luminescence GQDs are prepared by a microwave-assisted hydrothermal method. The sizes of prepared GQDs ranged from 5 to 8 nm. Fluorescence performance analysis showed that GQDs perform excitation-dependent PL behaviors, which are same with the carbon quantum dots. The research shows that with the increase of the microwave time and microwave power, the fluorescence intensity of GQDs first increased and then decreased. When the GO sheets were under 500 W for 5 min, the intensity got the strongest. While the solvothermal temperature has no effect on the fluorescence emission wavelength of the graphene quantum dots, the fluorescence emission spectra red shifts as the microwave treatment time is increased. The study of the quantum confinement effect of the GQDs is currently under way. The discovery of the new PL from GQDs may expand the application of graphene-based materials to other fields such as optoelectronics and biological labeling.

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