

Structural and Optical Evolution of Graphene Oxide under X-Ray Irradiation: Insights from UV-Vis and FTIR Spectroscopy

Peikai Wu^{12*}, Hongwei Li³⁴

¹*Department of Radiation, Heyou Hospital, No.1, Fosan, China*

²*School of Physic, University Sains Malaysia, Pulau Pinang, Malaysia*

³*Department of Radiation Oncology, Changzhou No.2 People's Hospital, Changzhou, China*

⁴*Department of Medical Physics, Nanjing Medical University, Changzhou, China*

**Corresponding Author. Email: wpkzdz@outlook.com*

Abstract: With the development of the times, the importance of graphene oxide is becoming more and more obvious and is being applied to more and more aspects. The application of graphene oxide in the field of medicine is also developing, graphene oxide (GO) can be used for photothermal treatment of tumours through photothermal effect, GO can be used as a drug carrier and so on. This study focuses on the reaction of graphene oxide after X-ray irradiation. The GO samples were made into different concentrations and then irradiated with the irradiation parameters of 40Kv, 100mA, 1.0mAs, SID = 100cm, and the irradiated and unirradiated samples were subjected to UV-visible detection and FTIR detection. It was found that in UV-Vis detection, while the samples with concentrations of 1.0mg/ml, and were redshifted, which represents a reduction reaction of GO. In the FTIR assay, samples with 1.0 mg/ml concentration were selected for the assay because the samples were contaminated and it was found that the absorption peaks in the range of 3200-3600 cm⁻¹ and 1700-1750 cm⁻¹, 1000-1300 cm⁻¹ were significantly weakened or disappeared, which represents the removal of hydroxyl and carboxyl and epoxy groups. Based on the experiments, it can be known that the reduction reaction is carried out by reducing the oxygen functional groups in GO, which leads to the reorganisation of the carbon skeleton structure and the formation of more carbon-carbon double bonds, generating rGO. finally, rGO can be generated from GO after x-ray irradiation, but it is necessary to choose the appropriate energy and irradiation time.

Keywords: Graphene Oxide, Reduce Graphene Oxide, UV-Vis, FTIR

1. Introduction

1.1. Background

The term "graphene" was first coined by A. Geim and K. Novoselov, who were awarded the 2010 Nobel Prize for their discovery of a two-dimensional material with a thickness of a single carbon atom of high crystalline quality. They obtained the first monolayer and few-layer meta stable graphene nanosheets by mechanically exfoliating graphite samples [1][2].

Graphene oxide (GO) is a two-dimensional (2-D) monolayer graphite that is valued for its accessibility and material compatibility. It can be produced by mechanically agitating or ultrasonically treating graphite oxide to exfoliate it into lamellar flakes. GO and its derivatives are rapidly becoming the most studied carbon-based materials in many fields due to their high stability, two-dimensional planar structure, large surface area, ease of chemical adaptation through their functionality, efficient surface loading of many biomolecules, as well as optical, electrical and mechanical properties [3]. GO has attracted a lot of attention because of its ease of use and compatibility with many materials. GO is relatively inexpensive, physically robust and chemically stable due to the strong influence of C-C bonds in its structure [4]. In terms of material properties, graphene oxide and its reduced state show two different appearances. Graphene oxide is insulating and the oxidized groups (epoxy, C-O) and hydroxyl, C-OH) are removed by reduction [5]. The electronic structure of reduced graphene oxide changes from insulating to semiconducting by removing the oxidized groups, which are carboxyl (C-O) and hydroxyl (C-OH), and carboxy (COOH) and carbonyl (carbonyl (C=O)) at the boundary [6].

1.2. Atomic structure of graphene oxide

Graphene Oxide (GO) is a derivative of graphene produced by the oxidative treatment of graphite. From the picture below, it can be seen that the atomic structure of graphene oxide consists of carbon atoms in sp^2 hybridized orbitals to form a hexagonal honeycomb lattice planar film. The graphite layer of GO contains hydroxyl (-OH) and epoxy (-O-) groups on both sides and carboxyl (-COOH) groups on the edges. These oxygen-containing groups make it easy for GO to form modified graphene oxide (MGO) through covalent or non-covalent interactions with organic small molecules and polymers [7].

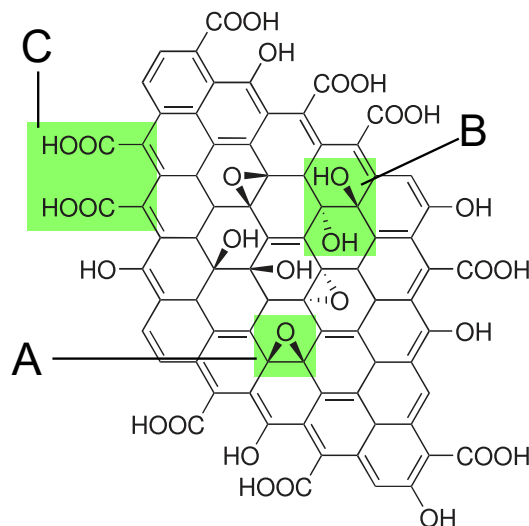


Figure 1: Structure proposed in 1998, contains functional groups: A: epoxy bridge, B: hydroxyl group, C: paired carboxyl group [8]

1.3. Comparison of graphene oxide and reduced graphene oxide

Graphene Oxide and Reduced Graphene Oxide are two different forms of graphene materials that differ significantly in their structure, chemical properties and applications.

Reduced Graphene Oxide (rGO) exhibits improved electrical conductivity compared to GO, although it remains inferior to pristine graphene. The reduction process partially restores the conjugated

structure of graphene by removing some oxygen groups, but the perfect lattice structure is not fully recovered.

The hydrophilicity of rGO is reduced, but the chemical stability and mechanical properties are improved. So GO is more used in composites and biomedical fields, while rGO is more suitable for fields such as electronic devices and energy storage devices due to its better conductivity and chemical stability [9].

2. Methodology

2.1. Materials

This experiment used a 0.8-1.2nm nano sized graphene oxide aqueous solution (concentration: 1mg/ml) purchased by Xi'an Qiyue Biotechnology Co., Ltd.

2.2. Experimental procedure

Uniformly coat 4 glass substrates with graphene oxide (GO) solution, and divide them into two groups after drying:

Exposure group (2 pieces): Siemens Multix Select DR (40 kV, 100 mA, 1.0 mAs/time, SID=100 cm) was used for 4 X-ray exposures, with a 5-minute interval between each exposure (in a room temperature and ventilated environment).

Control group (2 pieces): placed in the same environment but not irradiated.

One sample per group was used for UV-Vis (monitoring $\pi \rightarrow \pi^*$ transitions) and FTIR (analyzing functional groups) detection. All samples were subjected to spectral measurements before and after irradiation to track dynamic changes. "

3. RESULT

3.1. Results and analysis of UV-Vis

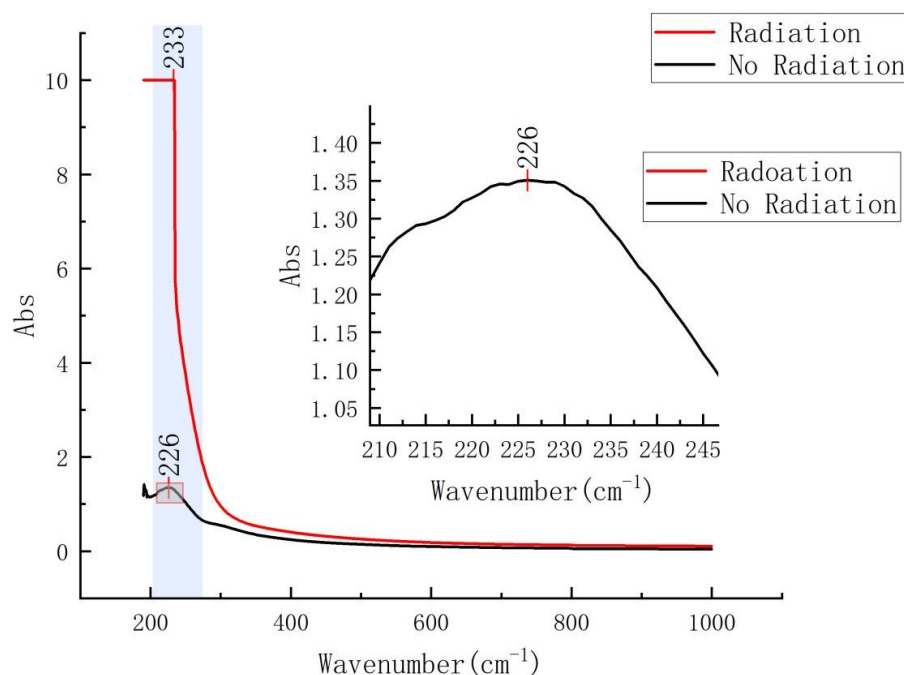


Figure 2: Comparative UV-Vis images of post-irradiation and unirradiated samples at a concentration of 1.0 mg/ml

The absorption peak after radiation treatment appeared at 234 nm. the absorption peak without radiation treatment appeared at 228 nm.

A slight change in the position of the absorption peaks after radiation treatment suggests a change in the GO structure, possibly due to a radiation-induced reduction reaction.

In Figure it is shown that the radiation-free sample has a high absorption at about 228 nm, while the radiation-treated sample has a diminished absorption around this wavelength. This change verifies that the radiation treatment led to the reduction of GO, reducing the oxygen functional groups (e.g., hydroxyl and carboxyl groups) and making the carbon backbone structure tend to be characterized by rGO.

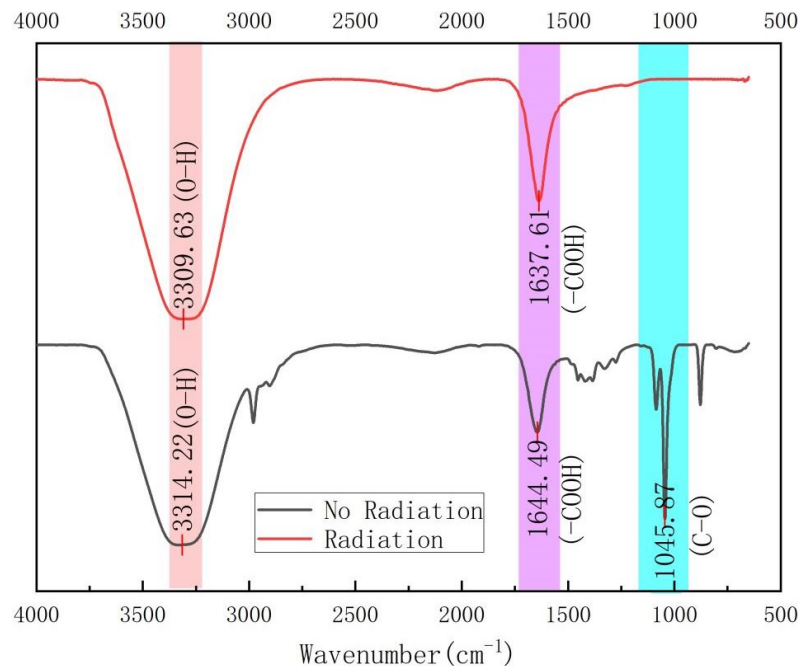


Figure 3: FTIR comparison images of post-irradiation and unirradiated samples at a concentration of 1.0 mg/ml

3.2. Results and analysis of FTIR

The absorption peaks at 3302 cm⁻¹, 1641 cm⁻¹, and 1044 cm⁻¹ were weakened in the radiation-treated samples as compared to those without radiation. This may indicate that the radiation resulted in GO reduction, reducing oxygen functional groups (e.g., hydroxyl and carboxyl groups).

4. Discussion

The characteristic absorption peaks of GO usually appeared in the 230-240 nm wavelength region, corresponding to the π - π^* leap.

The characteristic peaks of rGO usually appear in the wavelength region of 260-270 nm.

the samples with concentrations of 1.0 mg/ml were red-shifted. During the reduction process of GO, the oxygen-containing functional groups on the surface were removed, and the conjugated structure of the sp² carbon atoms was restored, and the increase in this conjugated structure led to a decrease in the energy required for the electron leaps, resulting in a red-shift of the absorption peaks.

In the case of the samples, the absorption peaks appear to increase substantially, and when GO is reduced to rGO, the removal of the oxidation groups leads to an increase in the sp² hybridization

between the carbon atoms, which enhances the absorption of the π - π^* leaps. This usually leads to an increase in absorption in a specific wavelength range.

Whereas rGO has a more complete conjugate structure than GO, the degree of electron delocalization is increased, leading to enhanced absorption in the visible and near-infrared regions. This enhanced absorptivity is usually expressed as an increase in absorbance.

The reduction process may lead to a decrease in the optical band gap of the material, allowing more photons to be absorbed by the material, resulting in an increase in absorbance. rGO's improved electrical conductivity also leads to an increase in absorbance, which also implies better absorptive properties. All of these reasons can lead to a large increase in the absorption peaks.

In the FTIR detection of GO, there are several major characteristic peaks of GO:

Hydroxyl group (-OH): in the range of $3200\text{--}3600\text{ cm}^{-1}$, there is usually a broad absorption peak indicating the presence of hydroxyl group.

Epoxy group (C-O): characteristic peaks in the range $1000\text{--}1300\text{ cm}^{-1}$ indicate the presence of an epoxy group.

Carboxy group (-COOH): a strong absorption peak occurs in the range of $1700\text{--}1750\text{ cm}^{-1}$ indicating the presence of carboxy group.

Carbon-carbon double bond(C=C): characteristic peaks in the range $1000\text{--}1300\text{ cm}^{-1}$ indicate the presence of a carbon-carbon double bond.

The main feature of rGO's on FTIR is the significant weakening or disappearance of the absorption peaks in the range of $3200\text{--}3600\text{ cm}^{-1}$ and $1700\text{--}1750\text{ cm}^{-1}$ in the FTIR spectrum of rGO as compared to GO, indicating the removal of hydroxyl and carboxyl groups. The absorption peaks in the range of $1000\text{--}1300\text{ cm}^{-1}$ are also attenuated, reflecting the removal of epoxy groups.

And on Figure 3, it can also be found that the absorption peaks in the range of $3200\text{--}3600\text{ cm}^{-1}$ and $1000\text{--}1300\text{ cm}^{-1}$ are significantly weakened or disappeared, which verifies the formation of reduced graphene oxide, as rGO is characterized by the reduction of oxygen-containing functional groups and the increase of carbon-carbon double bonds. However, we did not find carbonyl group (C=O) at $1700\text{--}1750\text{ cm}^{-1}$.

Finally, the combined results from UV-Vis and FTIR spectroscopy confirm the hypothesis that X-ray irradiation induces the reduction of graphene oxide. The observed shifts in absorption peaks and the weakening of characteristic FTIR bands indicate that X-ray treatment reduces oxygen functional groups, transforming GO into rGO. This reduction is crucial for modifying the electronic properties of GO, potentially enhancing its conductivity and making it more suitable for applications requiring graphene-like materials.

In this experiment, the improvement needed is to increase the exposure time and intensity of the sample, but due to the use of medical X-ray machines, this may lead to a series of problems such as insufficient response. Instruments capable of long-term stable exposure should be used to ensure more thorough reaction of the sample.

Since only UV-Vis and FTIR were used to test the samples in this experiment, there may be some errors, for this problem we can use Ramon spectroscopy, Scanning Probe Microscopy (SPM), X-ray Photoelectron Spectroscopy (XPS), Scanning Photoelectron Microscopy (SPEM), etc., which can help us to determine whether or not the samples are generating rGO. this can help us to be more sure of the results of the experiment. This way, we can be more sure of the accuracy of the experimental results.

5. Conclusion

This study aims to investigate the effect of X-ray irradiation on graphene oxide (GO). From the data obtained by UV Vis, it was found that the sample with a concentration of 1.0mg/ml after irradiation showed a red shift and a significant increase in the absorption peak. In addition, the reduction of

oxygen functional groups can confirm that the reduction reaction of GO has occurred, but it is uncertain whether rGO has been produced. Therefore, we need to perform Fourier transform infrared spectroscopy analysis on the irradiated samples.

After detecting the reduction of oxygen functional groups and the increase of C=C in the irradiated samples, it also indicates that the reduction reaction of the irradiated samples has taken place and rGO has been produced.

Finally, it is concluded that after a certain amount of X-ray irradiation, GO undergoes a reduction reaction and rGO is produced.

The significance of these findings lies in the potential applications of irradiated GO in various fields such as electronics, biomedicine, and environmental remediation.

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