Study on the surface modification and mechanism of multilayer graphene by ion beam irradiation

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Abstract
To improve the poor dispersion and insufficient interfacial adhesion of reinforced graphene (GN) in copper matrices, the graphene surface is irradiated with a Cu ion beam. To study the mechanism of surface modification of irradiated Cu+2 sample on the surface of graphene, the Raman spectroscopy, x-ray photoelectron spectroscopy (XPS), atomic force microscope (AFM), and transmission electron microscope (TEM) are employed. The results of Raman spectroscopy showed that the value of relative intensity ratio $I_D/ I_G$ of the characteristic peaks of unirradiated graphene was 1.2530 where it became 0.8693 after the irradiation process. It showed an 30.6% reduction in the ratio of $I_D/ I_G$ indicating that the ion beam irradiation reduces the surface defects of graphene and causes obvious modification effects. XPS results showed that the irradiated Cu deoxidizes with the epoxy, hydroxyl, or carboxyl group on the surface of the GN, resulting in Cu compounds attached to the surface of the GN. In addition, irradiation introduces stress on the graphene surface to promote the formation of a wrinkled structure to cause the surface morphology to change, as witnessed by the rougher surface morphology, as compared to the unirradiated area. The TEM results showed a recrystallization on the surface of the GN after the irradiation process. Moreover, it showed that the GN lattice was significantly qualified. Ion beam irradiation improves the quality of the surface of GN lattice, reduces the surface defects of graphene, and displays obvious modification effects.

1. Introduction
Since its discovery in 2004, graphene has become a research hotspot many scholars around the globe due to its unique honeycomb structure and excellent physicochemical properties, and has been widely used in biomedicine, flexible batteries, superconductors, polymer matrix composites, and other fields [1–3]. However, the graphene surface with a complete crystal structure is not active, which leads to poor dispersion in the metal matrix and insufficient interfacial adhesion with the metal matrix, which greatly limits further applications of graphene in metal matrix composites. At present, research on the surface functionalization of graphene is still in its early stages. The existing surface functionalization of graphene mainly includes covalent bond functionalization, noncovalent bond functionalization, element doping, and ion beam irradiation [4–6]. Ion beam irradiation is the process of accelerating ions and introducing them into the material surface to change the structure and properties of materials or using the interactions between ions and the material surface to change the material morphology. Ion beam irradiation technology provides advantages of low pollution, processing stress, deformation and high processing quality. It is widely used in the fields of material modification, microstructure fabrication, morphology modification and so on. Kim et al [7] used N+ as the irradiation source and energy to modify the graphene surface at 100 eV, annealed the single-layer GN and multilayer GN implanted with N+, and analyzed and compared the structural characteristics of the single-layer GN and multilayer GN modified by N+ implantation after annealing. It was found that nitrogen atoms exist in monolayer graphene in the form of pyrimidine nitrogen, and the modified monolayer graphene still shows characteristics of a p-type semiconductor. After modification, compared with the modified monolayer graphene, multilayer graphene acts
as modified nitrogen atoms and exists in a free form in multilayer graphene. Therefore, this shows that modified multilayer graphene is converted from an n-type to p-type semiconductor after annealing. Buchowicz et al \cite{8} used C $^+$ as an implanted ion with an incident energy of 35 keV. The structure of the single-layer graphene greatly changed and the hall mobility significantly decreased. Wang et al \cite{9} used metal gallium ions as the irradiation source and modified single-layer graphene with a 30 keV high energy ion beam. Single-layer graphene is used as the channel layer of the back gate transistor, and the nonlinearity of its I-V output curve is reduced. Al-harthi et al \cite{10} used argon ions as the irradiation source and bombarded graphene with low-energy (1 keV) ion beam. As a result, the folded structure appeared on the surface of modified graphene in different amplitudes and periods, causing the electronic state in graphene to change from a sp$^2$ to sp$^3$ orbit. It has been shown that ion irradiation at a certain energy level can change the electronic hybrid structure in graphene, which then affects its electronic performance. Tapaszto et al \cite{11} used Ar $^+$ as the bombardment ion to study the changes in electronic structure caused by defects and dislocation. Scanning tunneling microscopy was used to compare the changes in graphene after bombardment, and it was found that the atomic structure of the bombarded sample was broken and formed a curved corrugated shape, which significantly affected the Fermi velocity. Compagnini et al \cite{12} used C ions as the bombardment target, accelerated C $^+$ with ultra-high energy (500 keV) to inject it into graphene stored on the silica matrix, and tested the modified sample by Raman spectroscopy and AFM. It was found that the modified sample had point defects. Qin et al \cite{13} used Si as the bombardment target to modify the GN. Results showed that Si would replace the carbon atoms in GN and the carbon atoms were knocked out by Si atoms with increasing bombardment energy. Results also showed that the ion beam method can break some chemical bonds on the surface of graphene oxide, control the surface modification degree of graphene oxide by controlling the irradiation capacity and dose, make the material surface flatter, reduce surface defects, and improve the lattice quality of graphene oxide.

In this paper, Cu $^+$ sputtering modification experiments were carried out on the surface of graphene with the Cu target. The injection of Cu $^+$ increases the surface defects of graphene breaks the C$-$C, C$-$O and C=O bonds in graphene, deoxidizes the reaction between Cu and oxygen, improves the wettability of graphene, and increases the wrinkled structure and conductivity of the graphene surface. The crystallization of graphene was observed by transmission electron microscopy (TEM). At the same time, the effects of different irradiation energy and irradiation time on the surface modification of graphene were discussed, and the surface defects and modification mechanism of graphene were theoretically analyzed by Raman, x-ray photoelectron spectroscopy (XPS), atomic force microscope(AFM), transmission electron microscope(TEM) and other characterization methods.

2. Experiment

2.1. Preparation of irradiated graphene samples
Graphene is purchased from Guangzhou Amy graphene company, and the purity is greater than 97%. The preparation process of irradiated graphene is as follows: First, graphene is mixed with absolute ethanol in a certain proportion and then placed into an ultrasonic instrument for ultrasonic dispersion for 30 min. The dispersed graphene solution was dropped onto a 10 mm $\times$ 10 mm silicon wafer with a dropper and the sample was dried in a vacuum oven at 40 °C for 30 min.

2.2. Cu ion beam irradiated samples
The prepared graphene sample is placed in the chamber of a high vacuum magnetron sputtering, and the vacuum degree of the irradiation target chamber is (1.3–1.1) × 10$^{-3}$ Pa, argon flow rate is 30 sccm, and Cu target is selected as the target. By ionizing argon and bombarding Cu target, Cu atoms are introduced into the material surface to achieve the modification effect. Next, the sample was rotated, and the sample table was

| number | Power (W) | Argon flow rate (sccm) | Irradiation time (min) |
|--------|-----------|------------------------|------------------------|
| Process 1 | 30 | 30 | 10 |
| Process 2 | 40 | 30 | 10 |
| Process 3 | 50 | 30 | 10 |
| Process 4 | 60 | 30 | 10 |
| Process 5 | 50 | 30 | 5 |
| Process 6 | 50 | 30 | 15 |
| Process 7 | 50 | 30 | 20 |

Table 1. The parameters of experiment.
opened to allow for the sample to sputter evenly. The sputtering temperature was room temperature to prevent the influence of thermal energy on the surface quality of the graphene. Specific process parameters are shown in table 1.

2.3. Sample characterization
At room temperature, the surface morphology of graphene was observed by X130 scanning electron microscopy (SEM) produced by Philips in the Netherlands, and elemental analysis of the graphene surface was carried out by energy dispersive spectroscopy (EDS). The samples was characterized by Raman spectroscopy with a wavelength of 532 nm and a laser power of no more than 2 mW. The test condition of the Thermo ESCALAB 250Xi x-ray
photoelectron spectroscopy (XPS) was a vacuum degree of less than \(6.67 \times 10^{-7}\) PA, voltage 15 kV, current 10 Ma, and scanning mode CAE. The test probe of the atomic force microscope (AFM) adopts monocrystalline silicon and its working mode adopts a non-touch style. Before and after modification, the graphene was characterized by a Tecnai G2–20 transmission electron microscope (TEM) of American FEI company at an accelerating voltage of 200 kV.

### 3. Results

#### 3.1. SEM analysis

Figure 1 is an SEM image of graphene sputtered by a Cu ion beam. Figure 1(h) shows the surface morphology of the original graphene. The graphene surface is relatively smooth and there are few folds. Figures 1(a)–(d) is a SEM diagram with a sputtering power of 50 W and times of 5, 10, 15 and 20 min, respectively. It can be seen from the figure that the existing forms of Cu on the graphene surface vary greatly with increasing sputtering time. It can be seen from figure 1(a) that Cu forms a thin film on the graphene surface. Compared with figure 1(h), there are folds on the graphene surface and many copper particles are adsorbed. The formation of copper particles is because the sputtering time is short and the energy deposition is not enough to break more bonds, which leads to the aggregation and growth of copper atoms on the graphene surface. In figure 1(b), as the thickness of the Cu film increases, the folds increase and the copper particles decrease. This is because energy deposition can cause Cu atoms to break the bonds in graphene and fill more defects, so Cu atoms will not aggregate and grow. Due to the long sputtering time and excess energy of Cu atoms, it can be seen from figures 1(c) and (d) that when the sputtering time is 15 min and 20 min aggregation occurs to form large particles attached to the graphene surface with uneven distribution and size. Figures 1(e), (f), (b), and 1g are SEM images with sputtering times of 10 min and sputtering powers of 30, 40, 50, and 60 W, respectively. Compared with figure 1(h), it can be seen from figures 1(e) and (f) that when the sputtering energy is low, there are few copper atoms deposited on the graphene surface, and the graphene surface is relatively smooth without wrinkles, which proves that the energy is too low to generate enough stress and form wrinkles in the graphene. At this time, the surface morphology of graphene cannot be changed. With increasing power, it can be seen that the surface structure of graphene has changed greatly and the fold structure has significantly increased, which is caused by the stress introduced to the graphene.
surface by the injection of Cu atoms. Figure 1(g) shows that excessive sputtering energy leads to the aggregation and growth of copper atoms and uneven particle size, which seriously affects the surface structure of graphene.

3.2. EDS and XRD analysis

Figure 2 shows the energy spectrum with an irradiation power of 50 W and irradiation time of 5 min. It can be seen from the figure that there is a Si peak and the atomic ratio of Si is about 11%, because GN is dispersed on the silicon wafer on the silicon substrate, and GN is thin, resulting in the energy spectrum probe hitting the silicon wafer. The reason why the content of copper is so low is mainly due to the short sputtering time and low energy. The existence of oxygen can prove that the surface of GN may contain copper oxide and cuprous oxide. In order to further prove the existence of CuO and Cu2O on the surface of GN, XRD test shows that there are CuO and Cu2O diffraction peaks in GN. Specific process parameters are shown in table 2.

| Spectrum | C     | O     | Si    | Cu    |
|----------|-------|-------|-------|-------|
| EDS1     | 84.31 | 3.73  | 11.15 | 0.81  |
| EDS2     | 84.16 | 3.49  | 11.68 | 0.68  |
| EDS3     | 83.40 | 4.58  | 11.06 | 0.96  |
| EDS4     | 84.10 | 3.34  | 11.92 | 0.64  |

3.3. Raman spectroscopy analysis

The Raman spectra of samples with different irradiation energy, power, and irradiation time were characterized. The results are shown in figure 3(a) below. It can be seen from the figure that both D peak and G peak are Raman characteristic peaks of C atomic crystal, which are near 1300 cm\(^{-1}\) and 1580 cm\(^{-1}\), respectively. The D peak represents the characteristic peak of lattice defects of the C atom, the G peak represents the in-plane stretching
vibration of the sp$^2$ hybrid of the C atom, and 2D peak appears at about 2700 cm$^{-1}$. The appearance of the 2D peak proves that the sample is multilayer graphene, and the 2D peak is a unique peak of graphene [14]. Generally, the ratio $I_D / I_G$ of the intensity ($I_D$) of the D peak to the intensity ($I_G$) of the G peak is used to measure the surface quality of the sample. The larger the ratio of $I_D / I_G$, the more defects in the C atomic crystal, and vice versa [15].

Table 3. Elemental contents in GN/Cu-GN.

| Samples | Contents of elements/% | Atomic ratio O/C |
|---------|------------------------|-----------------|
|         | C 1s       | O 1s    | Cu 2p |          |
| GN      | 94.26      | 5.74    | 0.061 |          |
| Cu-GN   | 87.77      | 9.49    | 2.74  | 0.108    |

Figure 4. XPS spectrum of graphene before and after modification: (a) total spectrum; (b) Cu 2p orbital diagram; (c) fitting diagram of original GN oxygen; (d) Cu-GN oxygen fitting diagram; (e) C peak diagram of original GN; (f) C peak diagram of modified graphene.
It can be seen from figure 3(a) that the peak of Cu$_2$O appears around 518 cm$^{-1}$, which may be due to the incomplete reaction between a small amount of Cu and the residual oxygen-containing functional groups on the surface of the graphene during sputtering, from which Cu$_2$O is produced. Compared with the non-sputtered graphene, the defect peak D intensity of the sample after sputtering increases in varying degrees, and the defect peak intensity increases the most at 5 min and 20 min due to the short sputtering time, thereby causing more vacancies than filled vacancies at 5 min, so the defect peak D intensity will significantly increase. When sputtering for 20 min, a large number of C atoms will be knocked out, and the structure of graphene will be seriously damaged. In comparison, when the sputtering time is 10 min, the increase in defect peak D peak intensity is the smallest, and the surface quality of the sample is better. Figure 3.

Figure 3(b) is a broken line diagram of the I$_D$ / I$_C$ values of samples with a sputtering power of 50 W and sputtering times of 5, 10, 15 and 20 min, respectively. It can be seen from the figure that compared with the non-sputtered graphene, with the increased sputtering time, the I$_D$ / I$_C$ ratio first increases, then decreases, and then increases sharply. The I$_D$ / I$_C$ ratio of the sample sputtered for 10 min is the smallest, which is 0.8693, and the I$_D$ / I$_C$ ratio of the non-sputtered graphene is 1.2530, which is reduced by 0.3837, which is reduced by 30.6%, Therefore, it is proved again that the surface quality of the sample with sputtering time of 10 min is the best. Figure 2(C) is the Raman diagram of different power sputtering for 10 min, where the Raman characteristic peak intensity decreases with increasing irradiation energy, which is consistent with the research results of prevel B [16]. In the figure, the intensity of defect peak D of the curve with sputtering power of 50 W increases the least, which may be because the sputtering energy is too small, and most of the sputtered Cu atoms have not reached the energy to generate vacancies on the graphene surface. In previous SEM characterization, it was found that there are many Cu atoms adsorbed on the graphene surface, which further proves that the sputtering energy is too low, and most of the Cu atoms have not been sputtered on the graphene surface. Only a small amount of Cu atoms are sputtered onto the graphene surface to produce vacancies. In the figure, the D peak intensity of the 60 W and 40 W sputtered defect peak is larger than that of non-sputtered graphene. The higher intensity of peak D may be due to the more vacancies produced by sputtering than filled by Cu atoms. The D peak intensity of 50 W defect peak is much lower than that of 40 W and 60 W, which proves that the surface quality of 50 W sample is relatively good.

Figure 3(D) is a broken line diagram of I$_D$ / I$_C$ with different sputtering power. With increasing sputtering power, I$_D$ / I$_C$ first decreases, then increases, then decreases to the minimum value, and finally increases. The I$_D$ / I$_C$ ratio of 50 W / 10 min is the smallest, which is 0.8693, and the I$_D$ / I$_C$ value of non-sputtered graphene is 1.2530. It is confirmed that the surface quality of graphene with a sputtering power of 50 W and time of 10 min is the best.

### 3.4. XPS analysis

XPS is commonly used to detect the valence and composition of elements on the surface of materials [9]. Therefore, the electron binding energy of Cl$s_{284.6\text{ eV}}$ was used as the internal standard to determine the content of various elements on the surface of the samples before and after sputtering modification, as shown in table 3. The change in elemental content in GN and Cu-GN can also be seen in the table. Compared with GN samples, the content of the C element in Cu-GN at 50 W / 10 min decreased and the content of O increased.

Figure 4(a) is the full spectrum of Cu-GN. The spectral results show that the modified GN surface contains Cu. The 2p spectrum peak of Cu in the sample shown in figure 4(b) shows that the binding energy of Cu element is 932.6 eV. It can be seen from the figure that when the valence of Cu element changes from 0 to 1$^+$ or 2$^+$, Cu2 p3 and Cu2 p1 will split to produce vibration peak positions. Therefore, Cu in 50 W / 10 min Cu-GN has absorption peaks at 931.8, 933.8, 941.2, 954.1, 962.4, and 952.2 eV. The change in the characteristic peak position of Cu indicates that the deoxidation reaction occurs between Cu and the oxygen-containing bond on the surface of graphene (copper atom breaks the bond of oxygen on the surface of graphene and reacts with oxygen to form copper oxide or cuprous oxide), which changes the valence of Cu. Figure 4(c) is the fitting diagram of oxygen element peaks in the oxygen-containing functional groups of GN. It can be confirmed again that the oxygen-containing groups of GN include O=–C–O, C–O–C and –OH. Figure 4(d) is the oxygen element fitting diagram of Cu-GN. Comparing the changes in the binding energy of each oxygen element group in the non-sputtered GN sample in table 4, it can be seen that the binding energy of O=–C–O, C–O–C and –OH in Cu-GN all shift to the low field direction, indicating that the oxygen element obtains electrons in the coordination reaction, which also proves once again that the deoxidation reaction occurs between Cu element and the oxygen in the oxygen-containing bond on GN, resulting in the fracture of the chemical bond [17]. Figure 4(e) is the intensity diagram of the C peak of the original graphene, and its peak intensity is close to 1.75 × 10$^4$. Figure 4(f) shows the intensity diagram of C peak of graphene after Cu sputtering modification, and its peak intensity is close to 1.5 × 10$^4$. The intensity of the C peak decreased after Cu atom sputtering modification, and the content of C in the original graphene decreased from 94.26% to 87.77%. It can be shown that some C was replaced by Cu in the sputtering process.
The graphene with sputtering energy of 50 W and time of 10 min was characterized by atomic force analysis. The results are shown in figure 5. Figure 5(a) is the morphology without sputtering and figure 5(d) is the sputtering morphology. Compared with figure 5(a), the surface morphology of figure 5(d) becomes rough. The change may be due to the deoxidation reaction between Cu and the epoxy, hydroxyl, or carboxyl groups on the surface of GN, resulting in the fracture of chemical bond. The resulting complex is attached to the GN surface, and the atoms on the GN surface are reduced. From the height interface diagram of figure 5(b) and figure 5(e), it can be

**Figure 5.** AFM images before and after graphene sputtering: (a) unsputtered GN surface; (b) figure A line chart of the position of the red line; (c) figure A three-dimensional diagram of the position of the red line; (d) GN surface map after sputtering; (e) figure D line chart of the position of the red line; (f) figure D three-dimensional map of the position of the red line.

### Table 4. Binding energy of oxygen in GN/Cu-GN.

| Samples   | O1s        | Binding energy/eV |
|-----------|------------|-------------------|
| GN        | C–O, C–OH | 531.03            |
|           | O = C–O   | 533.46            |
| Cu-GN     | CuO        | 529.7             |
|           | Cu2O       | 530.6, 530.7      |

3.5. AFM analysis

The graphene with sputtering energy of 50 W and time of 10 min was characterized by atomic force analysis. The results are shown in figure 5. Figure 5(a) is the morphology without sputtering and figure 5(d) is the sputtering morphology. Compared with figure 5(a), the surface morphology of figure 5(d) becomes rough. The change may be due to the deoxidation reaction between Cu and the epoxy, hydroxyl, or carboxyl groups on the surface of GN, resulting in the fracture of chemical bond. The resulting complex is attached to the GN surface, and the atoms on the GN surface are reduced. From the height interface diagram of figure 5(b) and figure 5(e), it can be
seen that some folds appear on the initially flat surface of GN after Cu sputtering. Figure 5(c) and (f) are the three-dimensional morphology of GN without sputtering and after sputtering respectively. Compared with figure 5(c), the morphology of fold structure can be seen more intuitively from figure 5(f), because strain will be introduced into graphene during Cu sputtering. According to the research of Lu [18], because the implanted ions have energy, internal stress will be introduced into GN, so the folded structure will be formed on the surface of GN. Using Ar$^+$ as the irradiation source, Hrthi et al [19] studied the implantation of argon ions into GN by ion beam irradiation technology, observed the structural changes of GN surface, and found that the fold structure was gradually formed in GN. In summary, the modified GN surface is attached with Cu derivatives, and there are many folds on the surface, resulting in changes in morphology and increased roughness.

3.6. TEM analysis

To further explore whether the microscopic morphology of Cu ion beam sputtered graphene changes, transmission electron microscopy was used to characterize the graphene after sputtering and the graphene without sputtering. The results are shown in figure 6. As seen in figure 6(a), the graphene raw materials that have not been sputtered are seriously amorphous due to technological problems in the preparation process, and it is difficult to find a complete lattice region. It can be seen from figure 6(b) that an obvious crystallization region appeared on the GN surface. According to the study of F. Rossi [20], the reason for the phenomenon of crystallization is that the irradiated ion energy deposition and ion beam irradiation cause the recrystallization effect of the irradiated sample. Therefore, the crystallization phenomenon observed in TEM images should be related to the thermal effect of ion beam irradiation energy deposition. It can also be seen from figure 6(b) that some areas do not have crystallization, which may be due to the different contents of epoxy bond, hydroxyl group and carboxyl group in the surface area. Figure 6(c) is the diffraction spot diagram of figure 6(b). First, we need to calibrate the camera constant K. Given the electronic wavelength $\lambda = 2.51 \times 10^{-3}$ nm and the effective length of the camera is 200 mm, the camera constant $K = \lambda A = 5.02 \times 10^7$ nm$^2$, starting from the minimum circle radius in figure 6(c), $R_1, R_2, R_3$ and $R_4$ were 2.818 mm, 3.402 mm, 4.604 mm and 5.496 mm, $d_1 = K/R_1, d_2, d_3$ and $d_4$ were 0.1781 nm, 0.1475 nm, 0.1090 nm and 0.0842 nm, respectively. The $d_{hkl}$ of Cu is 0.18080, 0.12780, 0.1090, and 0.08293 nm, respectively. The values of the two groups are close to each other, and the

![Figure 6](image_url)
The corresponding crystal plane index is (200), (220), (311), and (331). \( K_i = R_i d_{hkl} \) for \( K_1, K_2, K_3 \) and \( K_4 \) were calculated to be \( 5.10 \times 10^5 \), \( 4.35 \times 10^5 \), \( 5.02 \times 10^5 \) and \( 4.56 \times 10^5 \) nm, respectively, and \( K_5 = 4.76 \times 10^5 \) nm², as shown in table 5. Second, the ratio analysis method was used to analyze the diffraction spots. \( R_i^2 \) was calculated first, and \( R_1^2, R_2^2, R_3^2 \) and \( R_4^2 \) were 7.94, 11.57, 21.20 and 30.21 mm², respectively. The polycrystalline ring diffraction patterns \( R_i^2 / R_1^2 \) of Cu-based materials were 1, 1.46, 2.67 and 3.80, respectively. \( 3R_i^2 / R_1^2 \) are 3, 4.38, 8.01 and 11.4, respectively. By looking up the ratio rule of \( R^2 \), it can be known that the ratio rule of the face-centered cube is 3, 4, 8, 11 and 12. According to the above data, polycrystalline electron diffraction is face-centered cubic. Accordingly, the calibration can be shown in table 6.

### 4. Conclusion

1. Raman spectrum results show that GN with irradiation energy of 50 W and irradiation time of 10 min has the best surface quality. The relative intensity ratio of unirradiated graphene characteristic peak \( I_D/I_G \) is 1.2530, the relative intensity ratio of irradiated graphene characteristic peak \( I_D/I_G \) is 0.8693, and the \( I_D/I_G \) ratio decreases by 0.3837. The result shows that ion beam irradiation can reduce the surface defects of graphene and has obvious modification effect.

2. XPS results show that the irradiated \( Cu^+ \) reacts with the epoxy bond, hydroxyl group or carboxyl group on GN surface to form \( Cu \)-containing compounds attached to GN surface. After irradiation, impurities formed on the graphene surface and stress introduced on the graphene surface promoted the formation of fold structure and changed the surface morphology, and the roughness of the surface morphology was higher than that of the unirradiated region.

3. TEM results show that the surface of GN is crystallized after irradiation, and the lattice quality of GN is improved. The diffraction spot calibration shows that the crystallization phenomenon is caused by the energy deposition of the irradiated ions caused by \( Cu^+ \) sputtering and recrystallization effect of the irradiated samples.

### Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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