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Nitrogen-doped graphene prepared by high-temperature carbonization of polydopamine film

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Abstract: *Inspired by the mussel sticky protein, polydopamine (PDA) has attracted wide attention due to its extremely strong adhesion ability, unique biocompatibility and hydrophilicity, which can be conformally coated on almost all materials. In addition, due to its excellent carbon production rate and excellent structural control capabilities under inert gas, PDA is also used as the source of carbon nanomaterials, its derived carbon materials are used in front-edge fields such as flexible electronics, energy storage. In this paper, polydopamine was carbonized at 800℃ and explores the structure of PDA after carbonized. It is found it forms a structure of nitrogen doped graphene.*

Keywords: *polydopamine, high-temperature carbonization, nitrogen doped graphene*

1. Introduction

The surface of two-dimensional graphene crystal is smooth and inert, its chemical properties are very stable, its interaction with other media is weak, and there is a strong van der Waals force between graphene sheets, which is easy to agglomerate, making it difficult to dissolve in water and common organic solvents. In addition, the properties of graphene "zero band gap" semiconductors make their conductivity not completely controlled like traditional semiconductors, which greatly limits their further research and application. In order to make up for the defects of graphene, give full play to its excellent properties, and make it more widely used, in addition to the control of graphene morphology (size, shape and thickness), graphene must be effectively functionalized. The functionalization of graphene is an important means to realize the dispersion, dissolution and molding of graphene. Doping graphene is one of the important ways to realize the functionalization of graphene, which can effectively control the physical and chemical properties of graphene. At present, N atom (3.04), B atom (2.04) and P atom (2.19) with similar electronegativity (2.55) to C atom are mostly used for doping. Phosphorus doping rate is low, and the specific surface area of the doped material is small. After boron doping, the electronegativity of the material is smaller than that of nitrogen doping. However, nitrogen atom doped graphene can be used as an electron donor, which can make nitrogen doped graphene show more excellent properties than pure graphene. Therefore, nitrogen atom doped graphene plays a key role in expanding the application field of grapheme [1-6].

At present, the main methods of preparing nitrogen-doped graphene include chemical vapor deposition [7-9], solvothermal method [10], nitrogen plasma discharge[11], arc discharge[12] and microwave method[13-14], but these methods are relatively complex, and the preparation cost is relatively high. In this paper, the nitrogen-doped graphene was prepared by carbonizing the nitrogen-containing organic compound polydopamine at 800℃, and study for its structure.

2. Characterization and Result

2.1. Structural changes of polydopamine film before and after carbonization

According to Lee's method [15], we prepared the PDA films, and carbonized in a vacuum retirement furnace equipped with a temperature controller. The PDA film was heated from the room temperature to 800℃ at a heating speed of 10℃/min, and then annealing at 800℃ for 1 hour. We study the structure of the PDA film with the XRD diffraction (XRD), In the XRD diagram (Figure1 (a)) of the PDA film, a single peak appeared at about 22°at the 2θ value. That shows the orderly accumulation of a certain degree of PDA molecules in the reflection area of the graphite (002). The diffraction peak of the

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carbonized PDA film moves slightly towards a higher angle side.

The retention of the single -derivative peak in the XRD diagram of the carbonized PDA film shows that there is no major change in the laminar structure of the carbonized post -carbon. However, compared with PDA films, the carbonized PDA film shows a significant increase in structural order, and the diffraction peak has obvious sharpness, which shows that through carbonization, larger crystal size occurs. Figure1 (b) is the comparison of Raman spectrum before and after carbonization at 800°C. Through carbonization of 800°C, the intensity of the D and G peaks is significantly enhanced, the peak of the 1350 cm^{-1} originated from the spleen of the sp3 hybrid bond of the border or other defects. Low graphite microcrystalline orientation, incomplete microcrystalline, many structural defects, and unsaturated edges of carbon atoms lead to strong strength of the D peak. The G peak at 1580 cm^{-1} comes from the strong vibration generated by adjacent carbon atoms in the plane of the single crystal graphite mesh in the opposite direction. For vibration, its strength can be used to express the integrity of the sp2 hybrid key structure in the graphite structure. In the figure, the enhancement of the strength of the D and G peaks in the figure shows that the degree of graphitization is increased, there are also a large number of structural defects in the carbonized PDA film. The carbonized PDA film appeared obvious 2D peaks at 2700cm^{-1}, which indicates that graphene-like layered structure appears through high-temperature carbonization.

The area of 800 cm-1 to 1700 cm-1 in the Raman spectrum corresponding to the polydopamine film in Figure 1(b) is magnified. As shown in Figure1 (c), a clear peak appeared at 950cm^{-1}, which corresponds to the formation of PDA, but after the high temperature carbonization, the peak disappeared, and the strength of the D and G peaks increased, at the same time, a 2D peak appeared, which proved the carbonization process of the polyamine film. In the Raman spectrum of PDA film, you can also observe the D and G peaks, which shows that the PDA film has a certain graphite structure.

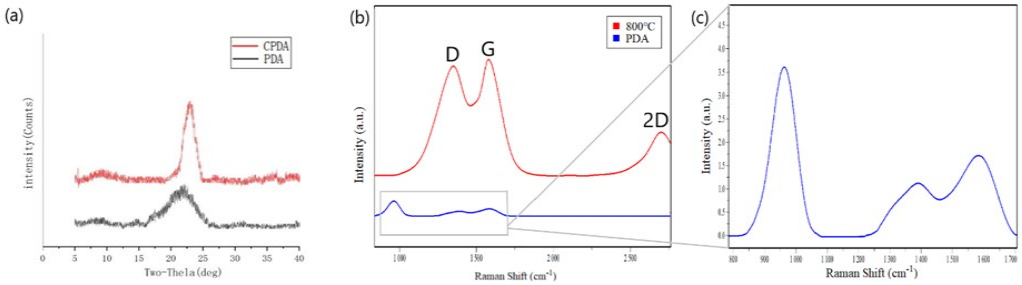

Figure 1: (a) X-ray diffraction images of polydopamine film before and after carbonization; (b) Raman spectra of polydopamine film before and after carbonization at 800℃; (c) Enlarged image of the region from 800 cm-1 to 1700 cm-1 in the Raman spectrum corresponding to the polydopamine film in Figure (b).

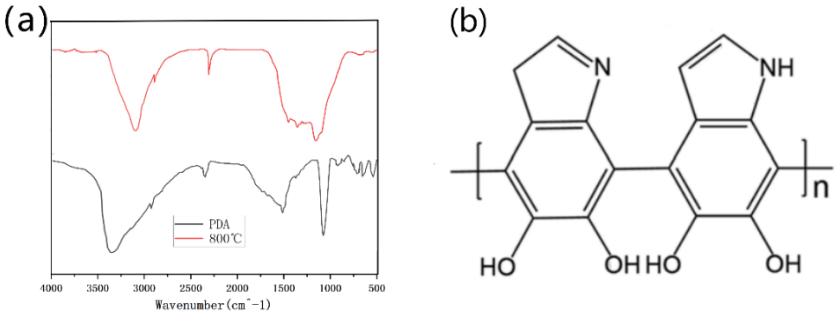

Figure 2: (a) ATR-FTIR spectrum of PDA film before and after carbonization at 800℃; (b) The structure of polydopamine produced by Dopamine auto polymerization.

Attenuated Total Reflection Flourier Transformed Infrared Spectroscopy (ATR-FTIR) was used to analyze the structure of the PDA film before and after carbonization at 800 ℃, as shown in Figure 2 (a). In the infrared spectrum of PDA, the band of 3500-3200cm^{-1} was derived from the stretching vibration of N-H and O-H, the peak at 2930-2880cm^{-1} was derived from the stretching vibration of C-H, and the peak at about 1500cm^{-1} was attributed to the C=N stretching vibration of indolequinone formed by dopamine self-polymerization and the skeleton vibration of benzene ring, The peak at 1050cm^{-1} is caused by bending vibration in C-H plane. According to the results of ATR-FTIR, the structure of the polyamine produced by the self-polymerization of dopamine is speculated. As shown in Figure 2 (b), in the process

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of polymerization, the C-H on the diagonal of the dopamine benzene ring breaks and combines with each other to form a cascade, and the amino group on the branch chain removes different number of H atoms to form C=N or C-N and combines with the broken bond on the adjacent corner to form a five-member ring. This is consistent with the conclusion put forward by Bernsmann et al. [16] in 2011 that "the formation of polyamine is similar to the way of synthesizing melanin".

Compared with the ATR-FTIR spectra of the original and carbonized polydopamine films, it can be observed that the structure of polydopamine undergoes obvious structural changes after pyrolysis: at 3400-3500cm-1, the stretching vibration from N-H and O-H obviously disappears. The peaks near 3150cm-1 and 2900-2850cm-1 come from C-H stretching vibration. The strong peak at 1500cm-1 C=N stretching vibration and the skeleton vibration of benzene ring. The peak at 1400cm-1 indicates the existence of N heterocyclic stretching vibration. The peak value at 1150cm-1 comes from the bending vibration in the N-H plane of the heterocycle. Combined with the results of ATR-FTIR spectrum, the structure of the carbonized polyamine film is speculated. The results are shown in the figure below. Figure3 (a) shows the overall structure of the carbonized polyamine film. At high temperature, the nitrogen-containing five-membered ring of polyamine breaks and crosslinks, making the overall structure of polyamine change into N-doped graphene, and some catechol groups may change into conjugated C=O (Figure3 (b)), Some molecules are partially crosslinked by C-O-C bond during carbonization (Figure3. (c)).

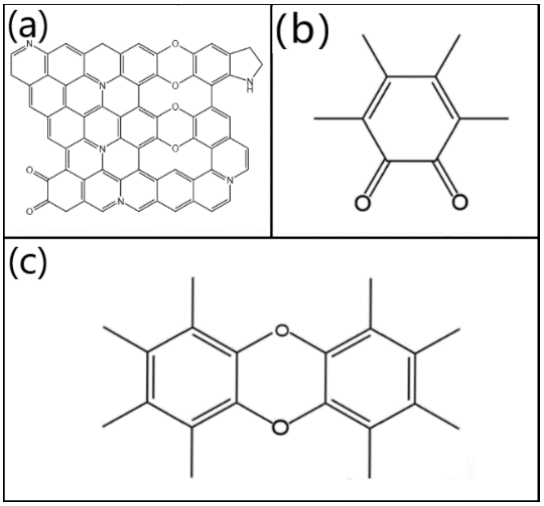

Figure 3: (a) The overall structure of the carbonized polydopamine film; (b) Conjugated C=O structure formed after carbonization; (c) C-O-C bond cross-linking formed after carbonization.

2.2. Changes of element content of polydopamine film before and after carbonization

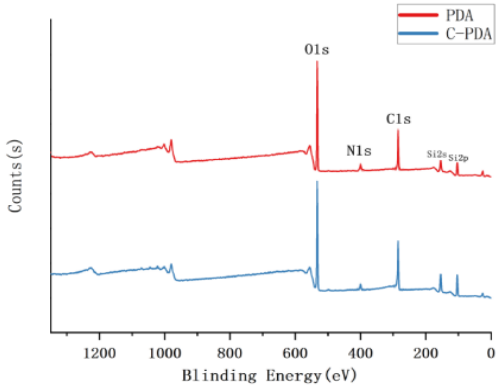

Figure 4: X-ray photoelectron spectroscopy of polydopamine film before and after carbonization at 800℃.

X-ray photoelectron spectroscopy (XPS) was used to analyze the element composition and content, chemical state, molecular structure and chemical bond of the polyamine film before and after carbonization at 800 ℃. The red curve in Figure4 (a) corresponds to the photoelectron spectrum of the

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pre-carbonized polyamine film, and the blue curve in Figure4 (a) corresponds to the photoelectron spectrum of the carbonized polyamine film. It can be observed that the intensity of O1s and N1s decreases after carbonization, while the intensity of C1s increases, which indicates that a certain amount of O and N elements are removed during the high-temperature carbonization of the polyamine film, However, it also shows that some groups containing O and N recombine to form relatively stable structures during high-temperature carbonization, and there are still O and N elements in carbonization products.

After removing the influence of silicon dioxide substrate, the content ratio of C, N, O elements before and after carbonization was analyzed. The oxygen (O) ratio decreased significantly, from 10.1% to 5.2%, and the nitrogen (N) ratio only slightly decreased, from 7.3% to 5.3%. This is also consistent with the conclusion obtained by comparing the energy spectrum before and after carbonization in Figure 5. Under vacuum conditions, some unstable O and N groups were lost through pyrolysis. Compared with N element, the change of O element content is more significant, which corresponds to the interaction of catechol group in the carbonization process of the polyamine film, and the dehydration and condensation between the OH groups on it forms C-O-C bond cross-linking, which significantly reduces the content of O element. The decrease of N element content is mainly due to the combination of certain N element with H free radical in the process of high-temperature carbonization and the release of NH_3.

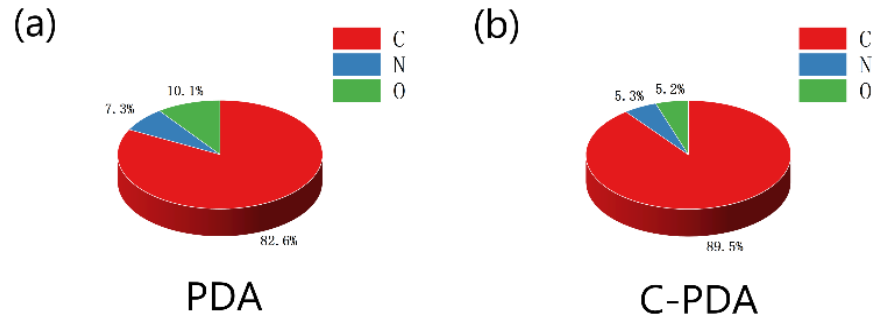

Figure 5: (a) Content ratio of C, N, O elements before carbonization; (b) Content ratio of C, N, O elements after carbonization.

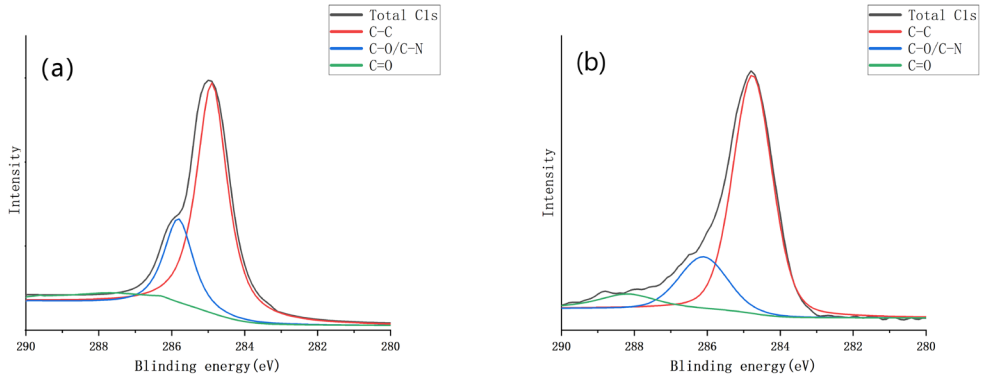

Figure 6: (a) C1s peak of non-carbonized polydopamine film; (b) C1s peak of carbonized polydopamine film

The C1s peak in the X-ray photoelectron spectroscopy of the pre-carbonized and post-carbonized polydopamine is analyzed. The energy spectrum of the C1s peak is shown in the figure. Figure6 (a) corresponds to the non-carbonized polydopamine film, and Figure6 (b) corresponds to the carbonized polydopamine film. It can be observed that in addition to the carbon peak generated by the carbon chain structure at 284.8eV, the polydopamine (PDA) has an obvious peak at 286eV, which mainly comes from the hydroxyl group contained in the polydopamine, With the carbonization of polyamine, the peak intensity of C-O at 286eV is weakened, and at 288eV, there is an obvious peak at the corresponding molecular structure C=O, which verifies the carbonized structure of polyamine obtained by ATR-FTIR spectrum analysis, the phthalic group of polyamine is converted into conjugated C=O during the carbonization process, or cross-linked through C-O-C bond.

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2.3. Change of film thickness before and after carbonization of polydopamine film

In the above figure, the intensity of the photoelectron spectroscopy Si2s and Si2p of the carbonized polyamine film has increased, which indicates that the thickness of the polyamine film has decreased during the carbonization process, resulting in more Si elements from the substrate. However, because the thickness of the polyamine film is only a few nanometers, the intensity change of the peak before and after carbonization is not significant. Therefore, the thicker polyamine film is obtained by increasing the self-deposition time of dopamine, and is heated from room temperature to 800℃ at the heating rate of 10℃/min according to the previous carbonization parameters, and then annealed at 800℃ for 1 hour to more clearly observe the thickness change during the carbonization of the polyamine film. The following figure shows the X-ray photoelectron spectrum of the thicker polyamine film before and after carbonization. The red curve in Figure 7 (a) corresponds to the pre-carbonization, and the blue curve corresponds to the post-carbonization. The Si2s and Si2p peaks are not observed in the photoelectron spectrum before carbonization, indicating that the film thickness of the polyamine film has exceeded the X-ray detection depth of the device, so that the silicon element on the silicon dioxide substrate cannot be detected.

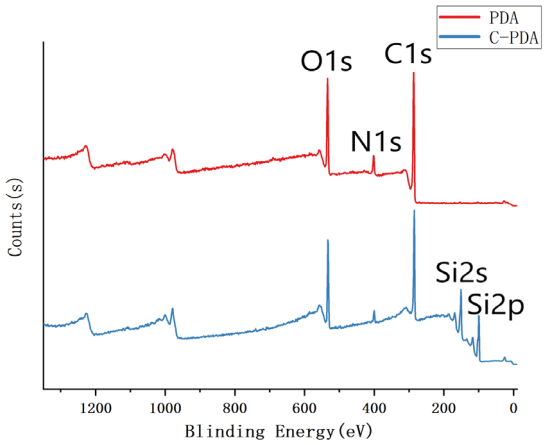

Figure 7: X-ray photoelectron spectroscopy of thicker polydopamine film before and after carbonization at 800℃

The strength of O1s and N1s decreased, the proportion of oxygen (O) decreased from 10.5% to 5.3%, and the nitrogen (N) decreased from 7.2% to 5.3% (Figure 8 (a) corresponds to pre-carbonization and Figure 8 (b) corresponds to post-carbonization), while the strength of C1s increased. The obvious Si2s and Si2p peaks appear in the X-ray photoelectron spectroscopy of the carbonized polyamine film, which indicates that there is obvious thinning in the carbonization process of the polyamine film, leading to the X-ray detection of Si element from the substrate.

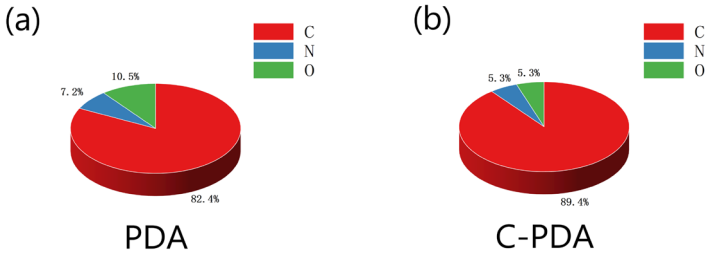

Figure 8: (a) Content ratio of C, N, O elements before carbonization; (b) Content ratio of C, N, O elements after carbonization

Scratches are made on the surface of the polydopamine film before and after carbonization. Figure 9 (a) is the sectional view of the line scan of the surface of the polydopamine film before carbonization by AFM, and Figure 9 (b) is the sectional view of the line scan of the surface of the polydopamine film before carbonization by AFM. It can be clearly observed that the concave area formed on the surface of the film by the scratch can be formed by the two. According to the depth of the concave, the thickness of the polydopamine film before carbonization is about 13 nm. The thickness of the carbonized polyamine film is about 8 nm, indicating that there is indeed a significant thickness reduction in the carbonization process of the polyamine film.

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The thickness reduction during carbonization is due to the removal of impurity elements and the development of membrane structure towards graphite-like structure under high temperature conditions, resulting in the reduction of the spacing between atomic layers. In the carbonization process of the polyamine membrane, the polyamine molecule is cracked, dehydrogenated, polymerized and cyclized at high temperature to form graphene-like structure. In this process, the dehydrogenation process and the polymerization process play a leading role. At the same time, these two processes are also important links to achieve the removal of impurity elements and the graphitization of the membrane structure.

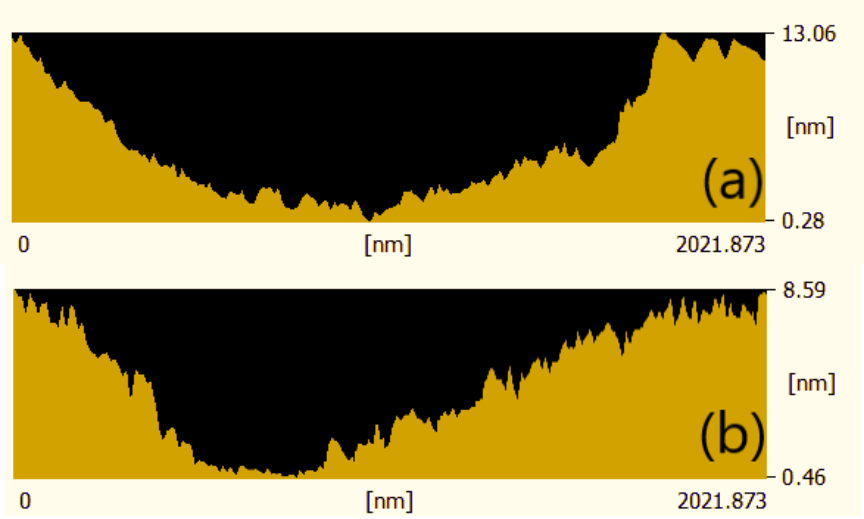

Figure 9: (a) Cross-sectional view of the scratch on the surface of the polydopamine film before carbonization; (b) Cross-sectional view of scratches on the surface of carbonized polydopamine film

3. Conclusions

The nitrogen-doped graphene can open the energy band gap and adjust the conductive type, change the electronic structure, improve the free carrier density, and improve the conductivity and stability of graphene [17-19]. In addition, introducing nitrogen-containing atomic structure into the carbon grid of graphene can increase the active sites adsorbed on the surface of graphene, thus enhancing the interaction between metal particles and graphene. Therefore, nitrogen-doped graphene used in energy storage devices has better electrochemical performance and is expected to develop into high-performance electrode materials. Existing research also shows that nitrogen-doped graphene can significantly improve the capacity characteristics, rapid charge-discharge capacity and cycle life of energy storage materials, and has great application potential in the field of energy storage [20-25].

We investigated the changes of molecular structure, chemical element composition and physical morphology (film thickness) of the polyamine film before and after high-temperature carbonization. Through high-temperature carbonization, the molecular layer spacing of the polyamine film will be reduced, and its catechol group will be converted into conjugated C=O during carbonization, or cross-linked through C-O-C bond, and the nitrogen atom in the gap position will enter the replacement position to realize the in-situ doping of nitrogen element, forming a relatively ideal nitrogen-doped graphene structure. However, compared with high-quality graphene materials, there are still many structural defects.

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