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Comparison of the amorphous/crystalline states of films made by oxidative self-polymerization and vacuum thermal evaporation using dopamine hydrochloride as a precursor

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Abstract: *The creation of carbon-based two-dimensional materials employing dopamine (DA) and polydopamine (PDA) as precursors is a fascinating and difficult research field [1, 2]. Due to its gentle reactions, high modification efficiency, excellent adhesion characteristics, and flexibility, PDA, which was inspired by mussel adhesion proteins, has a wide range of applications in nanocomposites [3-5]. In this study, films made by vacuum evaporation were found to 1) have a crystalline state compared to films created by oxidative self-deposition on the surface of silicon-based materials, and 2) have a higher bond stretching of the sp2 atom pair of the C atom (G-band) following carbonization.*

Keywords: *polydopamine, carbonization, vacuum evaporation, crystalline states*

1. Introduction

Currently, researchers might create a wide range of 2D polymers by methods involving hydrothermal, cycloaddition, self-assembly, and 2D templates. Despite the advances in research, it is still challenging to prepare 2D polymer films on a large scale. The three major challenges that the current development of 2D polymer materials is dealing with are 1) how to control the primary byproduct of 2D film preparation as a 2D structure rather than a 1D or 3D structure;2) how to reduce structural defects; and 3) how to prepare self-supported 2D films without the use of equipment. Dopamine (4-(2-aminoethyl)-1,2-benzenediol, DA) is a catechol compound that can be used in mussel biomimetic chemistry modification and whose molecular structure is rich in phenolic hydroxyl and amine functional groups[6], which can adhere to the surface of almost any material by its oxidative self-polymerization and can be used as a new precursor material for the preparation of carbon-based materials[7], using dopamine in a reactive solvent, oxidative auto-polymerization on the surface of silica-based materials to form PDA polymer films, which are carbonized to form nitrogen-doped (graphene-like) graphene[8].To manufacture two-dimensional nitrogen-doped carbon materials on SiO2/Si substrates, this research utilizes dopamine hydrochloride powder to form crystalline films on Si-based materials by vacuum thermal evaporation and carbonizes the films by vacuum thermal annealing.

2. Experimental

2.1. Preparation of thin films.

2.1.1. Film preparation by oxidative auto deposition

It is common practice to prepare polydopamine (PDA) by solution polymerization[9]. In an alkaline environment, the catechol functional group can deprotonate, principally dopamine (dopamine, DA), 5,6-dihydroxy indole, and pyrrole carboxylic acid three components, oxidation copolymerization to form oligomers, further through non-covalent contacts, thereby creating PDA[10-13]. Messersmith and LEE[3] initially described the oxidative self-polymerization of DA monomers to PDA in Tris buffer solution (pH = 8.5) at room temperature in 2007. They also employed 2 mg/mL of dopamine solution at pH 8.5 to alter the surface of a variety of organic and inorganic materials. After 24 hours of reaction, the PDA composite layer's thickness may reach about 50 nm. The PDA layers were deposited on the surfaces of noble metals, metal oxides, non-metallic inorganic oxides, polymers, and other materials. Polydopamine can be made using this straightforward, inexpensive process, however, the coated surface is vulnerable to the agglomeration phenomenon.

The color of the solution gradually changed from light brown to blackish brown during the reaction, as shown in Figure 1, implying the completion of polymerization. Experimentally, 0.375 g of dopamine hydrochloride powder was dissolved in 150 ml of Tris-HCL buffer (pH=8.5) (dopamine solution concentration 2.3 mg/ml), and the powder was dissolved quickly, and with time, a certain oxidation reaction occurred in the solution, which then triggered the self-polymerization and cross-linking of dopamine. Polydopamine contains a large number of phenolic hydroxyl and amino groups, which can adhere to almost any substrate surface, and the pretreated silicon oxide wafer sample was directly immersed in freshly configured dopamine solution and removed after 40 min reaction at room temperature to obtain a tightly adhered PDA layer on the silicon oxide wafer, which was dried overnight after blowing with nitrogen, and the thickness of the deposited PDA film was about 14 nm. A small number of agglomerates existed, and the presence of agglomerates increased the roughness of the film to some extent when the AFM test of surface roughness was performed, as shown in Figure 2.

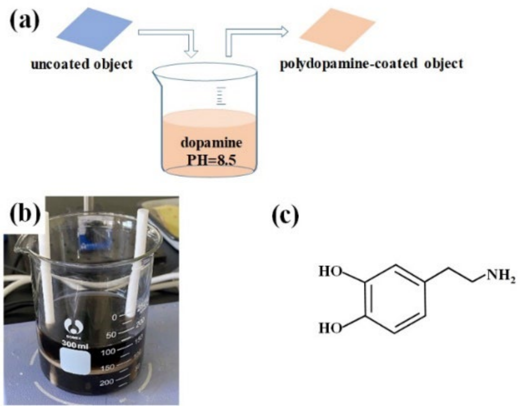


Figure 1: a) Schematic representation of dopamine deposition on the substrate, b) the optical photo of the dopamine polymerization reaction, and c) the molecular structure of dopamine.

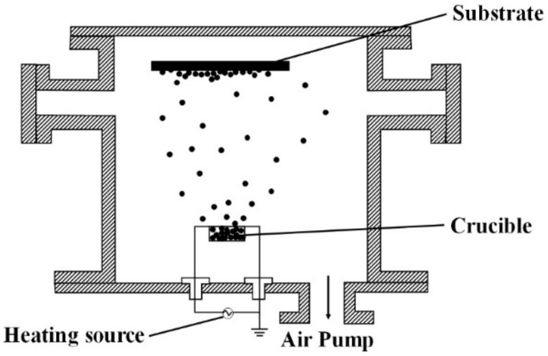


Figure 2: Schematic diagram of vacuum thermal evaporation coating process

Using the oxidative self-deposition method for film production, the whole process is completed in solution, and the modification of the oxidized silicon wafer surface is done in one step with simple operation steps and mild reaction conditions [14], while the conditions of the dopamine reaction solvent concentration, pH, temperature, and reaction time can be artificially changed to control the thickness of the polydopamine film on the oxidized silicon wafer substrate surface and reduce the agglomerated particles on the film surface.

2.1.2. Film preparation by vacuum thermal evaporation

The working principle of the vacuum thermal evaporation coating method is to evaporate the solid in the real environment so that it is converted into a gaseous state and finally deposited on the surface of the product to be coated. Dopamine hydrochloride, with a molecular weight of 189.64, is generally a white or off-white crystalline powder, the color will gradually darken when exposed to air or light, easily soluble in water, slightly soluble in anhydrous ethanol, with a melting point of 243~249 ℃.

The preparation of DA thin film on the silicon substrate is realized by thermal evaporation of dopamine hydrochloride powder in a vacuum. The vacuum thermal evaporation coating equipment is heated by using beam source furnace resistance, and the experiment controls the crucible temperature in the temperature range of 120℃-170℃, and when the evaporation rate tends to stabilize, it means that the surface components of dopamine hydrochloride powder evaporate out continuously in the form of atomic groups or ions, and then the baffle is opened to start formal coating, in a higher vacuum (pressure in the order of 10^-3 Pa), its gaseous particles in high can smoothly reach and settle on the surface of the coated substrate, through the scattered - island structure - lost structure - layer growth of the film formation process to form a thin film, in the silicon substrate attached and formed a uniform layer of DA thin film, the specific coating method flow details see Figure 2.

In this process, the film thickness vaporized is indirectly tested using the crystal wafer, and the thickness of the film deposited on the coated silicon substrate is deduced from the thickness of the film deposited on the crystal wafer when the position of the crystal wafer and the coated substrate are fixed. The vibration frequency of the crystal wafer has low sensitivity to temperature and is extremely sensitive to quality changes, and is used for film thickness detection in the vacuum thin film deposition process with high accuracy and good sensitivity. The approximate thickness of the film is deduced by recording the frequency change of the quartz crystal wafer during the vaporization process, and the specific formula for the change in crystal oscillation and film thickness is as follows:

$$\Delta f = -\frac{\rho_m f^2}{\rho_q N}\Delta d_m \tag{1}$$

Where: $\Delta \mathrm{f}$ is the amount of frequency change, ρ_m is the density of the film layer material, N is the frequency constant, f is the oscillation frequency, Δd_m is the amount of film thickness change, ρ_q is the density of the quartz crystal, and the negative sign indicates that the crystal oscillation frequency gradually decreases with the increase of the film thickness. OLED 4 serial research type multifunctional high vacuum coating machine with AT-cut crystal sheet and 6 MHZ frequency, as shown in Figure 3.

It was observed by optical microscopy that the thermal evaporation of dopamine first formed a structure of scattered dots on the silicon substrate material, and the scattered dots gradually connected to form an island-like structure on the surface of the substrate, and with increasing time, a thin film was formed on the substrate through further structural growth as well as layer-like growth. Comparing Fig. 4(a)(b), it is found that the arrangement of DA scattered dots on the silicon wafer is more regular compared to the oxidized silicon substrate after the evaporation of dopamine hydrochloride powder, the thin film structure on the silicon wafer has more "structural center points" layer structure. The thin films on silicon oxide wafers exhibit more "point-dispersion" structures Fig. 4(d), while the thin films on silicon oxide wafers exhibit more "line dispersion" structures Fig. 4(c).

DA films of ~11 nm were obtained by vapor deposition on oxidized silicon wafers with reduced surface roughness compared to PDA films prepared by oxidative auto-deposition.

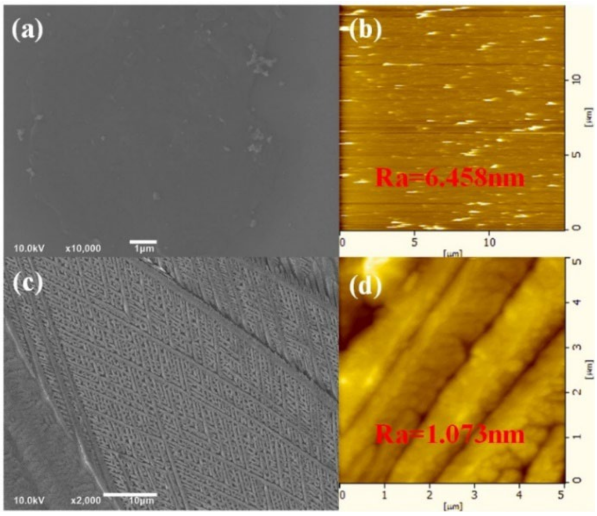
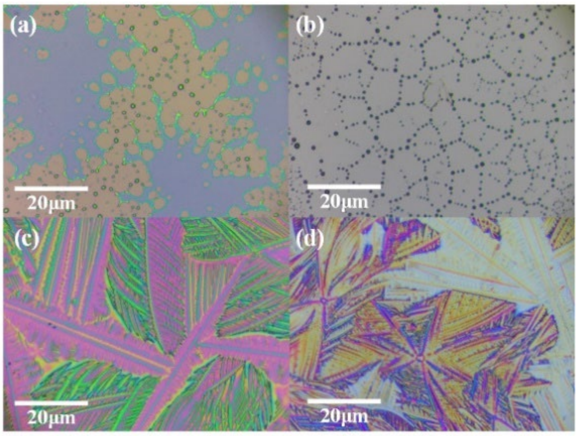


Figure 3: a) SEM characterization of PDA films prepared by oxidative auto deposition method and b) AFM characterization with film surface roughness Ra=6.458 nm. c) SEM characterization of DA films prepared by vacuum thermal evaporation method and d) AFM characterization, film surface roughness Ra=1.073nm

2.2. Carbonization of thin films

DA contains carbon and nitrogen and can introduce more Sp2-hybridized carbon atoms and highly electroactive nitrogen atoms in situ, thus carbon materials with high electrical conductivity and electrocatalytic activity can be obtained; the polymerization product of DA, PDA, as a special polyphenol substance, is rich in carbon and nitrogen elements and has good yields at high temperatures[15, 16], which can be used to generate N-doped carbon materials and achieve the effect of improving the electrochemical properties of carbon materials without introducing nitrogen elements to improve the electrochemical properties of carbon materials.



a) SiO2 substrate, evaporation temperature of 120°C and evaporation time of 120s; b) Si substrate, evaporation temperature of 120°C and evaporation time of 120s; c) SiO2 substrate, evaporation temperature of 120°C and evaporation time of 240s; d) Si substrate, evaporation temperature of 120°C and evaporation time of 240s.

Figure 4: Optical micrographs of thin films prepared on SiO2/Si substrates using the vacuum thermal evaporation method

The carbonization experiments of the films were divided into three control experimental groups.

Control experimental *Group I*: The PDA films prepared by the oxidative self-deposition method were carbonized at 800°C and 1000°C using a SiO2 sheet as the substrate. Firstly, the film samples deposited by the oxidative self-polymerization method were put into a quartz crucible, covered, and put into a vacuum annealing furnace with the vacuum maintained at about -0.1 Mpa, with 50°C as the starting temperature, ramped up to 800°C at 10°C/min and thermostated at this temperature for 60min, and left to drop to room temperature. The carbonized samples were named PDA/SiO2-800; with the same ramp up to 1000°C, the sample was named PDA/SiO2-1000, and the temperature change curve of the carbonization process was shown in Figure 5(a).

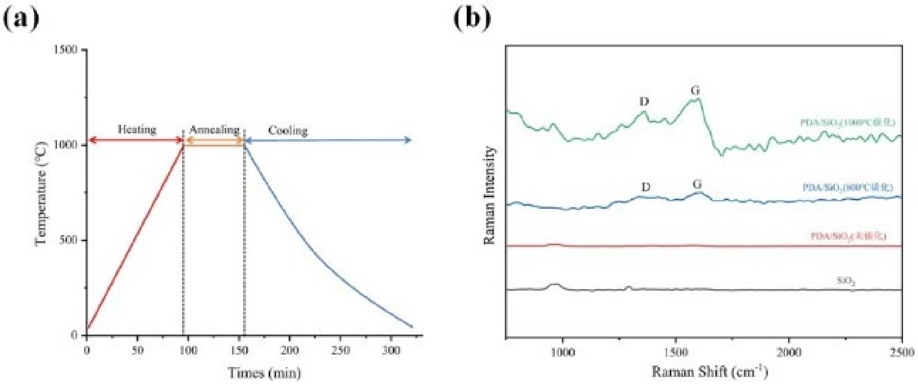


Figure 5: a) Schematic diagram of the temperature variation curve of the carbonization process; b) comparative Raman characterization of PDA films made by oxidative self-deposition before and after carbonization at different temperatures

The Raman spectra of the samples before and after carbonization were tested, in Fig. 5(b), the G bands representing the sp2 hybridization of C atoms appeared in the middle out of the tested spectra of

PDA/SiO2-800 and PDA/SiO2-1000, and the G peaks of PDA/SiO2-1000 were more obvious under the comparison of the two carbonization temperatures, so the carbonization of the DA films prepared by vacuum evaporation method was continued at 1000°C. The carbonized samples were named DA/SiO2-1000, and the comparative analysis with PDA/SiO2-1000 was performed as the control experimental *Group II*.

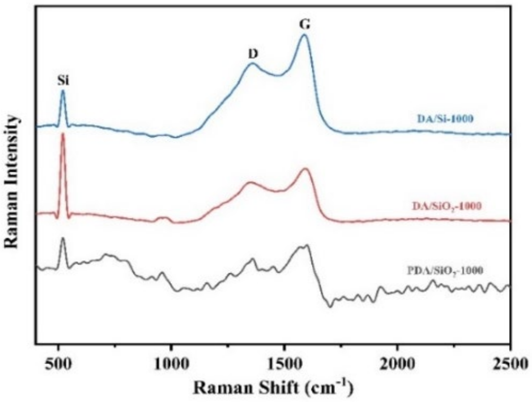


Figure 6: Comparison of Raman characterization after carbonization of PDA film prepared by oxidative self-deposition and DA film prepared by vacuum vapor deposition

Based on the observation of the structural surface, a slightly different laminar structure is present on the Si substrate and SiO2 substrate. Initially speculated that the difference in this structure will lead to a difference in the amount of DA adhesion on the substrate, so the DA film evaporated on the Si substrate will be carbonized under the same experimental conditions, the carbonized samples are named DA/Si-1000, compared with DA/SiO2-1000 as *Group III*. The results of Raman analysis after carbonization are shown in Fig. 6. It is found that the DA films on Si substrate have a more obvious G-band and weaker D-band after carbonization, and the Raman test results are smoother and the spectral peaks are more obvious compared with the PDA films prepared by oxidative self-deposition method.

3. Results and Discussion

3.1. Film surface coverage

The coverage of the films prepared by the vacuum vapor deposition method on the surface of the silicon wafer substrate is better than that of the silicon oxide wafer. In the experimental range of 120~170°C, the continuity of DA films on the oxide wafer substrate was not as good as that on the silicon wafer substrate, and localized unvaporized areas appeared on the oxide wafer, as shown in Figure 7(a), which did not appear on the silicon wafer (Figure 7(b)).

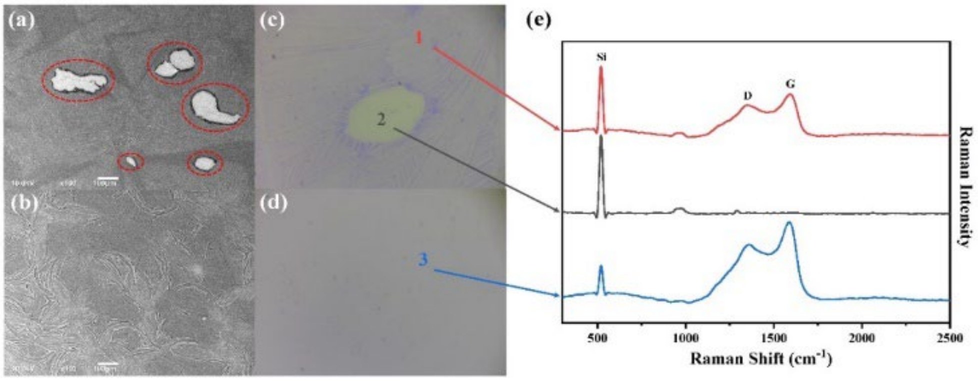


Figure 7: DA films prepared by vacuum vapor deposition on SiO2 substrate a) SEM characterization before carbonization and c) optical micrographs after carbonization at 1000°C; on Si substrate b) SEM characterization before carbonization and d) optical micrographs after carbonization at 1000°C; e) Raman characterization of the films in the corresponding areas in Figs. c) and d).

3.2. Crystalline analysis of the film

The crystalline properties of DA film materials obtained on different substrates were analyzed by X-ray diffraction (XRD), and the results are shown in Figure 8. DA films prepared by vapor deposition method on SiO2 and Si substrates showed Bragg peaks in the angular range of 0-65°, indicating that the samples contained crystalline components, while the XRD test of PDA films prepared by deposition method showed a large angular bulging in the range. Initially, it is assumed that the process of film preparation is related to the principle of oxidative self-deposition, which is a self-polymerization reaction of dopamine, and the reaction product is a polymer that does not generate polymer crystals without the induction of polymer colloidal seed crystals in solution. The vacuum evaporation process involves only physical changes, melting of dopamine hydrochloride powder, volatilization of hydrochloric acid, and sublimation of dopamine, which eventually adheres to the surface of the Si substrate. Figure 8 shows the XRD test results of DA films evaporated at 165°C on SiO2, Si substrate, and after comparing the two sets of data, it is roughly determined that the three strong peak positions of DA appear roughly at 27.4°, 32.8°, and 34.2°, and the positions of XRD peaks indicate the existence of structural ordering, similar to 2D carbon-based materials. In this way, it can also be determined that the dopamine film evaporated on the silicon-based material is a crystalline morphological film composed of C and N elements. It also provides a reference to the XRD Bragg peak position of dopamine.

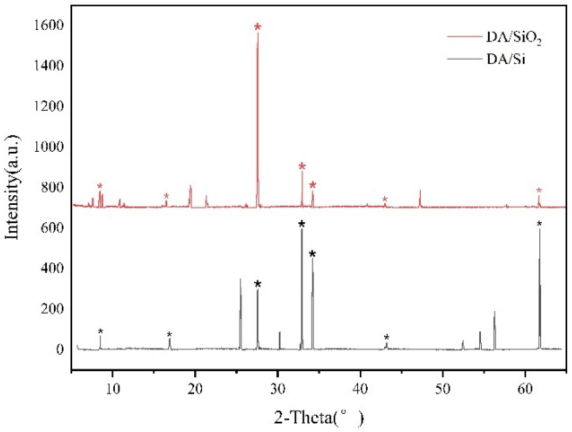


Figure 8: XRD characterization of DA films prepared on SiO2, Si substrates using the vacuum evaporation method

3.3. Post-carbonization film characterization

Each isotope of C has a distinguishable characteristic Raman spectrum, Raman spectroscopy is a fast, nondestructive, high-resolution method to characterize graphene, the G-band and D-band provide information about the structure of graphene and its mass, the G-band is located around 1580 cm-1, which comes from all sp2 bond-stretched carbon atom pairs in the ring and chain, recorded at 1350 cm-1 is the D-band, which can be attributed to the defects present in the structure with graphene. Using Raman spectroscopy to qualitatively characterize the thin film sample before and after carbonization, the spectrum of Si of the substrate appears at 520 cm-1 in spectrogram 7(e), the G-peak at 1580 cm-1 appears, corresponding to a specific C=C molecular bond vibration, and the spectral peak located at 1380 cm-1 corresponds to the D-peak, and the presence of the D-band indicates the presence of defects in the amorphous C or amorphous graphite layer. The sample is tentatively presumed to be a graphene-like structure after carbonization (formation of a partially graphitic structural layer or graphene oxide layer).

Raman spectroscopy is also very sensitive to the ordered state of carbon material structure, and usually the I(D)/I(G) value is used to respond to the degree of disorder or defect density of graphite layer in carbon material, the larger the I(D)/I(G) value, the less ordered the graphite layer and the higher the defect density, and vice versa, the more ordered the graphite layer and the lower the defect density. If the I(D)/I(G) value > 1, it means that the defects are larger and the content of amorphous carbon is higher, and vice versa indicates that the defects are less. the I(D)/I(G) value of PDA/SiO2-800 is about 0.82, the I(D)/I(G) value of PDA/SiO2-1000 is about 0.78, the I(D)/I(G) value of DA/SiO2-1000 is about 0.77, I(D)/I(G) values of DA/Si-1000 are about 0.72, I(D)/I(G) are less than 1, indicating that the PDA material, as well as the DA material, is more graphitized after carbonization as a carbon source, which is conducive to the electron conduction and electrochemical properties, while the I(D)/I(G) values of DA films prepared using the vapor deposition method are lower than those prepared by the oxidative self-deposition method, indicating that the I(D)/I(G) values of PDA films prepared by the vapor deposition method are lower than those of The I(D)/I(G) values of DA films prepared by vapor deposition are lower than those of PDA films prepared by oxidative self-deposition, indicating that the disorder induced by the rearrangement of carbon atoms during carbonization is lower in the films prepared by vapor deposition.

Both the films prepared by the oxidative self-deposition method and the vacuum evaporation method showed smoother coatings after carbonization than before carbonization, which may be caused by the reactions occurring during the carbonization process. XRD was again used to further determine the internal ordering of the two-dimensional films, and it was found that the XRD spectra after carbonization were very different from those of the original crystalline films, with bulging in a large angular range, as shown in Figure 9, indicating that the internal packing of the films was different from that in the original crystalline state and that the conversion from crystalline to amorphous composition was achieved in the film samples. The bulge appears in the ~10° position in the spectrogram, and the bulge in this position is a structural feature of amorphous SiO2, amorphous C, or graphene oxide. Analyzing the bulging degree of bulging on SiO2 and Si substrate around the ~10° position in the XRD test plot, the bulging on the Si substrate is more obvious than that on the SiO2 substrate, which weakens the influence of amorphous SiO2 on the surface, so it is tentatively speculated that the bulging at this position is more influenced by amorphous C. It is presumed that the amorphous C or graphene oxide structure appears in some areas after carbonization.

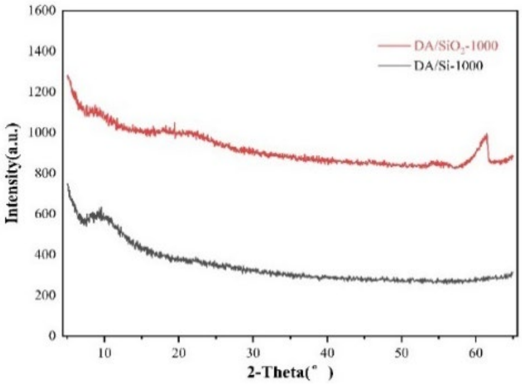


Figure 9: XRD characterization of DA films prepared on SiO2, Si substrate using vacuum vapor deposition method after carbonization at 1000°C

ATR-FTIR spectroscopy further characterizes the functional groups of pre-carbonization (DA/Si) and post-carbonization (DA/Si-1000) samples. When the components and molecules in the material are excited, the individual atoms or groups (chemical bonds) in the molecule produce characteristic vibrations, which lead to absorption at specific locations and exhibit vibrational energy levels, and the vibrations of the same type of chemical bonds are all very similar and always occur in a certain range. The whole infrared spectrogram can be divided into two zones, the 4000~1350 cm-1 zone is the absorption band produced by the stretching vibration, the spectrum is relatively simple but strongly characteristic, and the 1350~650 cm-1 is the fingerprint zone.

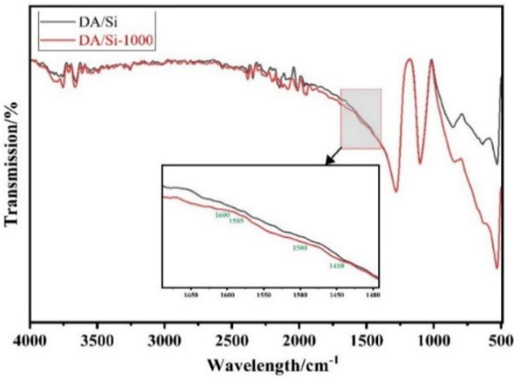


Figure 10: Preparation of DA films on Si substrate by vacuum evaporation method a) ATR-FTIR characterization before and after carbonization

The infrared absorption caused by the C=C bond stretching vibration in the benzene ring skeleton, in general, has four bands, about 1600, 1585, 1500, and 1450 cm-1, which can be used as one of the indications of the presence or absence of benzene ring. in the ATR-FTIR spectrum (Figure 10), there are absorption peaks in the region of 1600~1450 cm-1 before and after carbonization, and this region is the C=C of benzene ring skeleton vibration, it is assumed that the material has benzene ring structure before and after carbonization. After determining the basic skeleton of carbon, the low and high wave number regions were further compared and analyzed. In Fig. 11(a), the shoulder peak around 840 cm-1 is thought to be caused by the presence of substituents on the benzene ring, and the difference between this peak position before and after carbonization is not significant, indicating that the number and position of substituents on the benzene ring did not change due to carbonization.

The weak absorption peak around 3010 cm-1 (Figure 11b) is thought to be generated by the C-H stretching vibration of sp2 hybridized aromatics, which is more obvious before carbonization and disappears after carbonization. The carbonization process is generally accompanied by dehydrogenation, which is generally realized in the form of H2O molecules or H2, proving that the hydrogen atoms on the benzene ring achieve partial detachment; the three weak peaks from 3100 to 3010 cm-1, which are present before and after carbonization, are weaker in intensity after carbonization and are thought to be generated by the C-H stretching vibration.

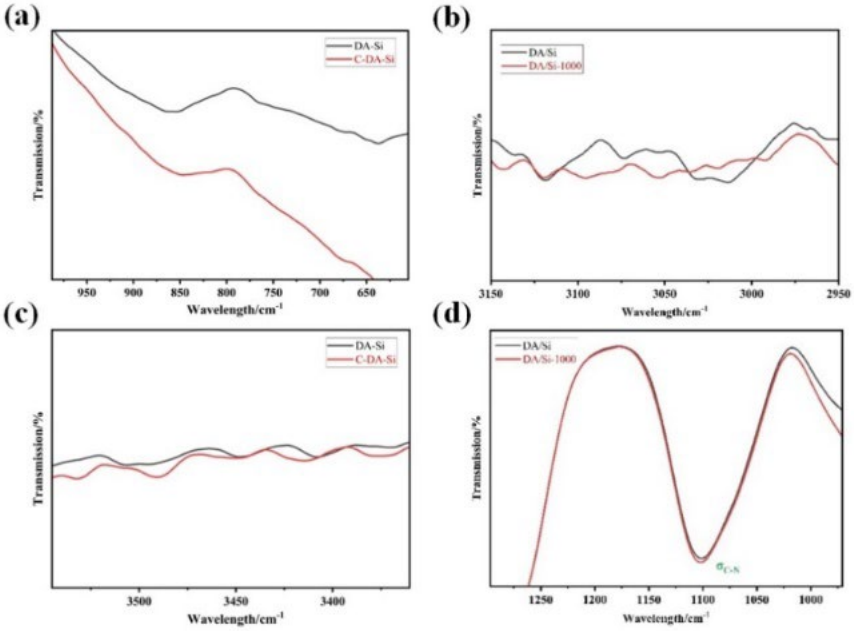


Figure 11: Local magnification of ATR-FTIR characterization before and after carbonization

The double peaks present at 3500~3400 cm-1 before and after carbonization (Figure 11c) are considered to be the stretching vibration of N-H, and the strong peaks at 1230~1030 cm-1 (Figure 11d) are presumed to be the stretching vibration sites of C-N. The stable existence of C-N bonds before and after carbonization ensures the effective doping of nitrogen elements.

4. Conclusions

In summary, this article outlined a straightforward approach: Dopamine (DA) films are self-supportingly attached via a vacuum thermal evaporation method on silicon-based substrates; these films have good homogeneity both before and after carbonization, and the characterization features of 2D carbon-based materials emerge following carbonization.

This method has several advantages over oxidative self-deposition for PDA films: 1) no agglomerated particles, which further reduces the film roughness; 2) short film-making time, and enables the preparation of crystalline films; and 3) reduced influence of impurity elements on the film-making during the chemical reaction, and the films have slightly better carbonization with lower I(D)/I(G) values. Additionally, it was established through experimentation that vacuum evaporation-prepared DA films on silicon wafers have a stronger carbonization effect than DA films evaporated on oxidized silicon wafers. All of these characteristics suggest that by regulating the right vacuum thermal evaporation temperature and duration, more uniform and thinner crystalline layers can be prepared on silicon wafer materials, and it is possible to manufacture nitrogen-doped carbon-based 2D materials on silicon substrates by carbonizing them under annealing conditions at 1000 °C and higher temperatures.

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