

Article

In-Situ Catalytic Preparation of Two-Dimensional BCN/Graphene Composite for Anti-Corrosion Application

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Abstract: In-situ catalytic growth of two-dimensional materials shows great potential for metal surface protection because of the impermeability and strong interaction of the materials with metal surfaces. Two-dimensional hexagonal boron-carbon nitrogen (h-BCN) is composed of alternating boron, carbon, and nitrogen atoms in a two-dimensional honeycomb lattice, which is similar to graphene. The corrosion caused by defects such as grain boundary of two-dimensional materials can be weakened by dislocation overlap via the transfer method. However, two-dimensional composite films prepared using the transfer method have problems, such as the introduction of impurities and poor adhesion, which limit their corrosion resistance. In this study, a layer of BCN/Gr two-dimensional composite was directly grown on the surface of copper foil using the CVD in-situ catalysis method, and its anti-corrosion performance was characterized by electrochemical and salt spray experiments. The results showed that the directly grown two-dimensional composite had better adhesion to the substrate and the advantage of grain boundary dislocation, thus showing a better anti-corrosion capability.

Keywords: BCN/graphene composite; CVD; anti-corrosion



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1. Introduction

With developments in modern science and technology, industrial production requires metal materials with higher stability and service life; thus the development of surface protection technology for metals is of great significance. Traditional anti-corrosion methods, such as protective coatings and sacrificial anodes, require very thick coating materials, which cause problems such as environmental pollution and easy peeling [1–4]. Therefore, it is of great significance to develop novel anti-corrosion materials with strong corrosion resistance. Two-dimensional (2D) materials directly grown on metal surfaces are not only impermeable, but they can be closely combined with the metal surface, thus fully meeting the requirements of novel metal protective coatings [5–9].

2D materials refer to nanomaterials with ordered structures on 2D planes. Their atomic thickness gives them excellent mechanical properties and light transmittance [10–12]. Graphene, the first 2D material that could be controllably prepared in the laboratory, is a honeycomb hexagonal plane crystal formed by the arrangement of single-layer sp^2 hybrid carbon atoms. Due to its 2D honeycomb lattice arrangement, it shows excellent impermeability [13,14], an extremely high theoretical specific surface area ($2630 \text{ m}^2/\text{g}$) [15,16], excellent light transmittance ($\sim 97.7\%$) [11], high Young's modulus ($\sim 1 \text{ TPa}$) [17], and good oxidation resistance [18,19]. These properties play an important role in its anti-corrosion mechanism, making graphene an excellent candidate for anti-corrosion materials [20]. However, the excellent conductivity of graphene can also promote the occurrence of electrochemical corrosion reactions, which compromise its long-term anti-corrosion ability [1,21].

2D hexagonal boron-carbon nitrogen (h-BCN), a novel 2D structure composed of alternating boron, carbon, and nitrogen atoms in a 2D honeycomb lattice, has recently

attracted considerable attention. Although 2D h-BCN has a similar structure to graphene, h-BCN is an excellent insulator due to its wide band gap, and its strong B-N, B-C, and C-N bond cooperation gives it strong mechanical strength [22,23], good high-temperature oxidation resistance, and thermal stability, showing strong oxidation resistance at 900 °C [24,25]. Therefore, 2D h-BCN nanomaterials directly grown on metal surfaces have the potential to effectively prevent corrosion molecules from diffusing to the surface of the metal substrate, thus improving corrosion resistance [26]. However, it is difficult to prepare a large area of single-crystal 2D material using the CVD method, and grain boundaries with poor adhesion and weak bond cooperation are unavoidable, which are usually the starting points for corrosion reactions of 2D materials in corrosive environments [1,6].

In order to eliminate the influence of the grain boundary of 2D materials and improve their corrosion resistance, some research has been devoted to the preparation of single-crystal 2D materials, but they are generally grown on the surface of single crystal substrates, which is difficult to achieve in actual preparations and applications on large areas [27,28]. Overlaying several layers of 2D materials by transfer is one way to weaken the influence of grain boundaries through grain boundary interlacing [29]. However, the adhesion between 2D films is poor, and impurities and breakage are introduced during the transfer process, which seriously affects its anti-corrosion performance [30]. In order to improve the performance of 2D materials in corrosion protection, this work proposed a new strategy of in-situ catalytic growth of composite 2D films prepared using the CVD method for metal corrosion protection. The boron carbonitride/graphene (BCN/Gr) 2D composites prepared by in-situ growth not only had very strong interlaminar forces, but also realized the dislocation of the grain boundary, which alleviated the corrosion caused by the grain boundaries. Salt spray experiments, electrochemical tests, and adhesion measurements showed that the in-situ grown BCN/Gr 2D composite films had excellent adhesion and improved corrosion resistance. Compared with as-grown BCN film and the BCN-Gr composite prepared by the transfer method, the corrosion rate of in-situ grown 2D BCN/Gr film was reduced by 91.4% and 57.1%, respectively. Therefore, this work not only provides a new 2D material for corrosion prevention, but also provides new experimental and theoretical support for research investigating the corrosion prevention mechanisms of 2D materials.

2. Results and Discussion

A home-built CVD furnace was used for the preparation of the 2D materials, such as BCN and BCN/Gr, and its preparation diagram is shown in Figure 1a. As shown in Figure 1a, the growth process had two heating zones, including the sub heating zone at the front end of the quartz tube and the main heating zone at the rear section of the quartz tube. The temperature in the main heating zone was regulated by the electric heating parts of the CVD furnace, and the temperature in the sub heating zone was controlled by the heating belt wound on the quartz tube. When BCN and BCN/Gr two-dimensional films were grown by CVD, methane and borane ammonia were used as the precursors. After exhausting the air in the tubular furnace with Ar, the temperature of the main heating zone was raised to 1000 °C, the mixed gas of methane and hydrogen was introduced, and methane molecules were decomposed into carbon atoms. Then, the temperature of the auxiliary heating zone was set to 90 °C, and the borane ammonia was decomposed by heat to produce $\text{-BH}_2\text{-NH}_2\text{-}$, which diffused to the main heating zone with the gas flow, and then was further decomposed into -B-N- under the high temperature in the main heating zone [26]. Finally, -B-N- was deposited on the copper substrate and re-bonded into BCN films with carbon atoms. The preparation of BCN/Gr 2D composite films combines the growth process of graphene and BCN in the same procedure with copper foil was used as catalyst and borane ammonia and methane as precursors. The graphene layer was first grown on the copper foil surface with CH_4 as the carbon source. First, methane was decomposed and provided C atoms. Since Cu has poor affinity to C, C atoms could diffuse on the surface and build up the thermodynamically stable honeycomb lattice by surface

nucleation and growth [31,32]. Then, the temperature of the sub heating zone was raised, the borane ammonia precursor was added on the basis of the CH_4 source, the BCN layer continued to grow on the surface of the graphene film, and the BCN/Gr 2D composite film was finally obtained.

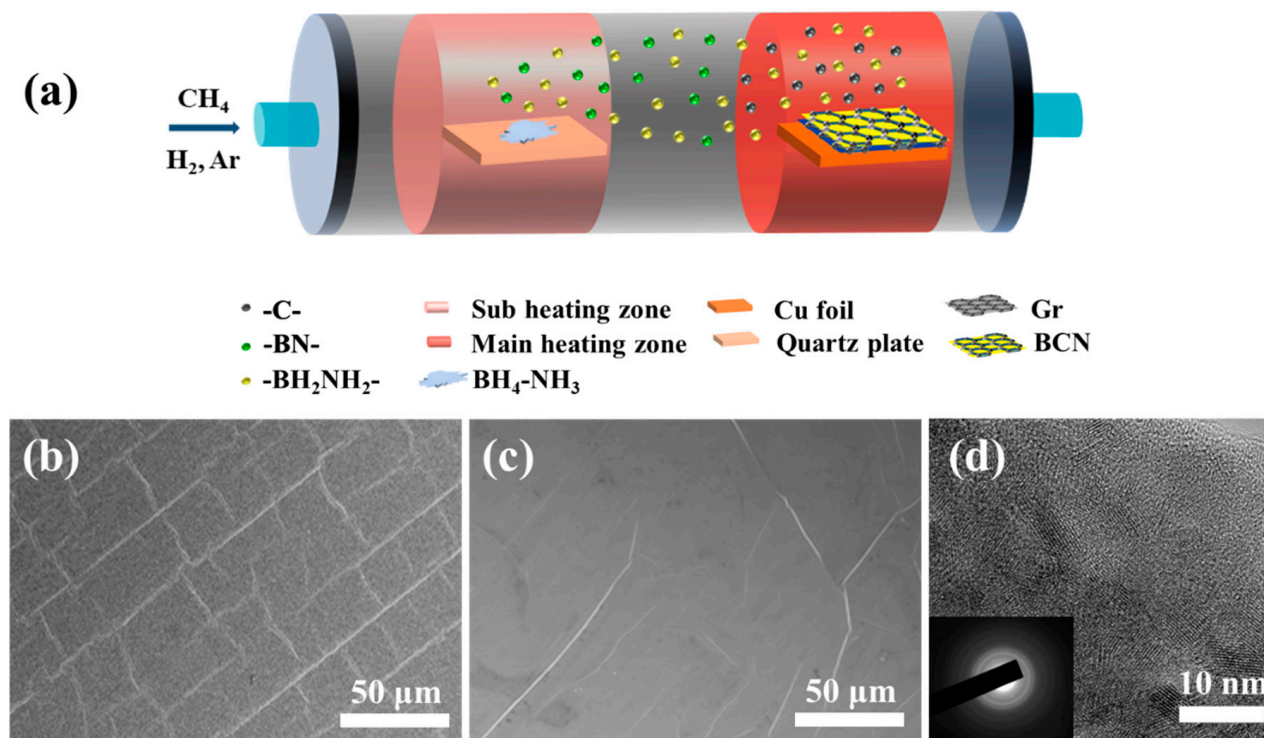


Figure 1. (a) Diagram of the home-built CVD furnace for the preparation of BCN and BCN/Gr; (b) SEM of the BCN two-dimensional film; (c) SEM of the BCN/Gr two-dimensional film; (d) TEM and electron diffraction pattern (inset) of the BCN/Gr two-dimensional film.

Figure S1 and Figure 1b,c show the SEM images of Gr, BCN, and BCN/Gr grown on Cu foils, respectively. It can be seen that the 2D films are continuous and complete, and there are a lot of wrinkles on the surface. These wrinkles may be due to the release of internal stress in the growth base (copper foil), which conforms to the characteristics of the 2D film [33]. In addition, the BCN/Gr 2D composite film shows (Figure 1c) a flatter surface structure than BCN (Figure 1b), which may be due to the reduction of copper foil roughness and the release of surface stress during the first step of growing the graphene layer. Figure 1d shows the TEM topography of BCN/Gr, which indicates that BCN/Gr is a complete continuous film and shows a clear laminar structure with irregular lattice distribution. As graphene grows below the BCN layer, it is difficult to directly observe the structure of the graphene layer. However, the clear laminar flow structure and staggered lattice shown in the TEM diagram may be derived from the interlacing of two different 2D structures (graphene and BCN). Among them, the electron diffraction pattern shown in the illustration in Figure 1d clearly shows the annular diffraction characteristics of BCN and Gr 2D structures [34–36]. Meanwhile, the EDS results also confirmed the even distribution of C and N elements in the as-prepared 2D film (Supporting Information Figure S2). The thickness of the in-situ grown BCN and BCN/Gr 2D films was characterized by TEM and AFM. The results showed that the thickness of the BCN 2D film was approximately 3–4 nm and the thickness of the BCN/Gr 2D composite film was 8–10 nm. The significant increase in the thickness of BCN/Gr may be due to the increase in the number of layers of BCN films grown on the graphene (Supporting Information Figure S3).

Raman spectroscopy and infrared spectroscopy are important characterization means to evaluate the bonding and structure of two-dimensional materials. In this study, we

analyzed the quality of BCN and BCN/Gr samples prepared at different growth times using these two techniques. Samples BCN1,2,3 and BCN/Gr1,2,3 represent samples with growth times of 10, 20, and 40 min, respectively. After etching the Cu substrate from the BCN and BCN/Gr layers by liquid phase etching (Supporting Information, Figure S4), the BCN and BCN/Gr 2D composite films were transferred to the surface of SiO₂ substrates for characterization. Figure 2a shows the Raman spectra of the BCN 2D films, showing wider D and G peaks, similar to those of graphene (Supporting Information, Figure S5). The shoulder peaks appearing at $\sim 1363\text{ cm}^{-1}$ corresponded to in-plane substitution, vacancy, or lattice distortion between grain boundaries in the sp^2 structure; and the peak at $\sim 1600\text{ cm}^{-1}$ reflected the tensile structural strength of sp^2 bonding [37]. Compared with graphene, the D and G peaks of the BCN 2D layer blue shifted to higher wavelength positions due to the combination of B and N bonds with C in BCN. For the infrared spectrum of BCN (Figure 2b), the peaks at 1392 cm^{-1} and 809 cm^{-1} were attributed to in-plane tension and out-of-plane bending vibrations of the B-C-N rings, respectively. The infrared peaks between 1070 and 1250 cm^{-1} indicated the existence of B-C bonds. The films rich in B had maximum absorption at $\sim 1100\text{ cm}^{-1}$, whereas the films rich in C had maximum absorption at $\sim 1250\text{ cm}^{-1}$ [22,38].

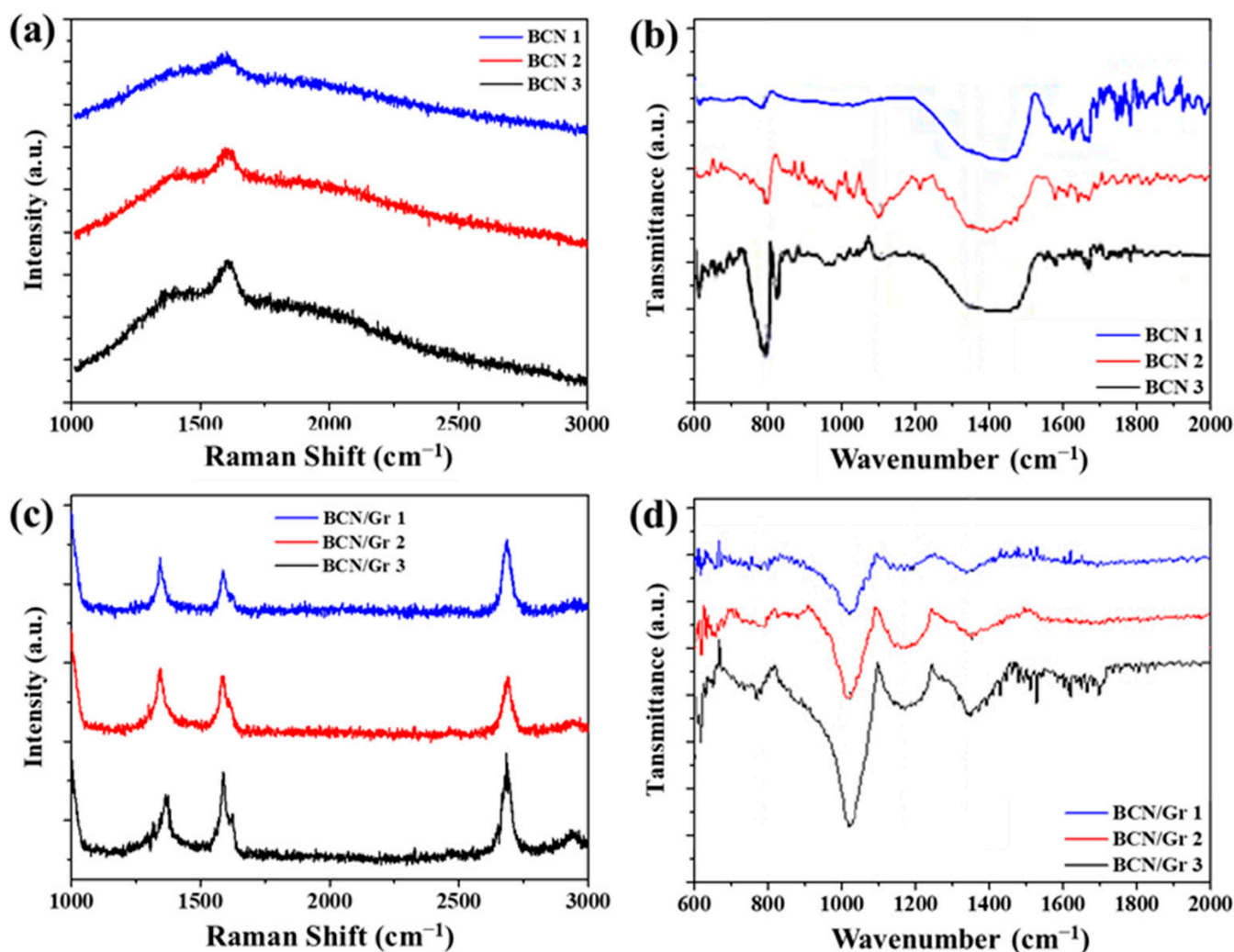


Figure 2. (a) Raman spectra of BCN two-dimensional films; (b) Infrared spectra of BCN two-dimensional films; (c) Raman spectra of BCN/Gr two-dimensional films; (d) Infrared spectra of BCN/Gr two-dimensional films.

Figure 2c shows the Raman spectra of the BCN/Gr 2D composite films. The characteristic peaks of graphene, such as G peaks and 2D peaks, are clearly visible. At the same time, the characteristic peaks of BCN can also be observed at $\sim 1363\text{ cm}^{-1}$ and $\sim 1600\text{ cm}^{-1}$. As the growth time increased, the G peaks gradually broadened, indicating that the peak strength at 1600 cm^{-1} was increasing and forming the wide characteristic peak of graphene. Meanwhile, the strength of the D peak was also gradually increasing, which proved that the content of BCN in the 2D composite films was increasing, thus confirming the formation of the BCN/Gr 2D composite material.

Figure 2d shows the infrared spectra of the BCN/Gr 2D composite films. It can be seen that in contrast to the infrared spectra of BCN (Figure 2b), the maximum characteristic peak of BCN/Gr (Figure 2d) moved to $\sim 1100\text{ cm}^{-1}$, which was attributed to B-C bonds. Meanwhile, with increasing growth time, the peak at $\sim 1100\text{ cm}^{-1}$ also increased, indicating the increasing B content of the BCN/Gr sample. The Raman and infrared spectra proved the successful preparation of BCN and BCN/Gr 2D composite materials.

It is reported that 2D materials protect the metal substrate through their impermeability and tight combination with the substrate [1,29,39]. However, two-dimensional film materials prepared using the CVD method have a large number of grain boundaries, which are considered to be the starting point of corrosion reactions. By transferring another layer of 2D film on its surface, the grain boundaries could be dislocated, thus preventing the diffusion of corrosion reactants to the metal substrate [29]. Therefore, we used the liquid etching method to transfer the BCN and graphene films onto the surface of an as-grown BCN/Cu foil surface and prepared BCN-BCN and BCN-Gr samples, respectively (Supporting Information, Figure S1). The graphene layer used for transfer was prepared using the CVD process, which is described in the Supporting Information (Figure S2). Figure 3a,c display schematic diagrams of the BCN-BCN and BCN-Gr samples, and Figure 3b,d shows their corresponding SEM results, respectively. As shown in Figure 3b,d, the boundaries of the transferred 2D films can be clearly observed. The transferred graphene and BCN films were relatively complete and not damaged during the transfer process. In addition, the BCN film (Figure 3b) was significantly thicker than the graphene film (Figure 3d). It can be seen that in this study, we prepared a variety of 2D films based on graphene, BCN, and BCN/Gr composite films through direct growth and transfer. In order to describe and characterize the samples more clearly, we summarized the samples and preparation methods in Table 1.

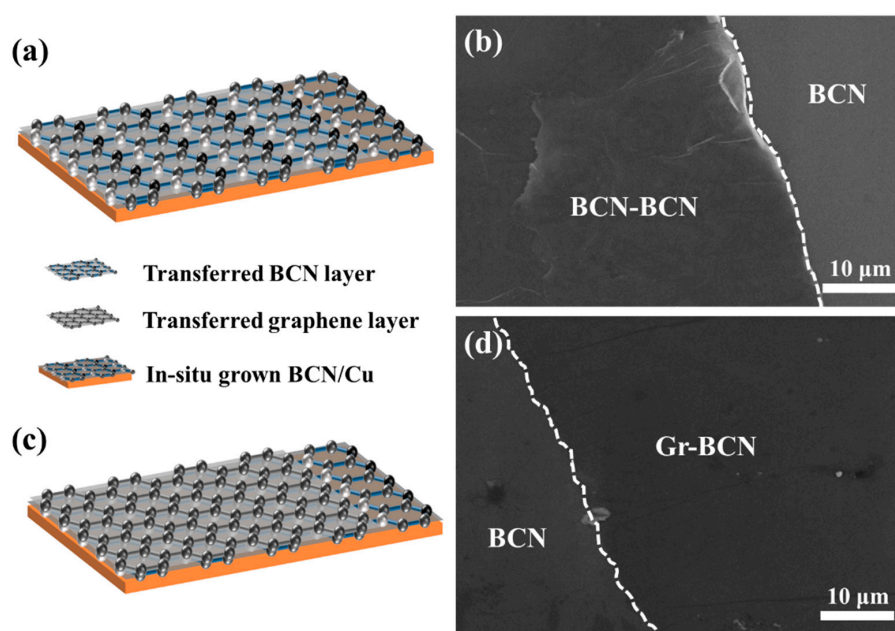


Figure 3. (a) Schematic diagram of BCN-BCN sample; (b) SEM of BCN-BCN sample; (c) Schematic diagram of BCN-Gr sample; (d) SEM of BCN-Gr sample.

Table 1. Samples prepared in this study.

Sample	Method	Growth Time of BCN (min)
BCN 1	CVD grown BCN	10
BCN 2		20
BCN 3		40
BCN/Gr 1	CVD grown BCN/Gr composite	10
BCN/Gr 2		20
BCN/Gr 3		40
BCN-Gr 1	CVD grown BCN + transferred BCN	10
BCN-Gr 2		20
BCN-Gr 3		40
BCN-BCN 1	CVD grown BCN + transferred Gr	10
BCN-BCN 2		20
BCN-BCN 3		40

Electrochemical testing is considered a convenient method to evaluate the corrosion resistance of protective coatings [40–42]. Figure 4a shows the schematic diagram of the three-electrode system for electrochemical testing, in which the platinum electrode is the counter electrode, the saturated calomel electrode is the reference electrode, the samples to be tested are the working electrodes, and the electrolyte is 5% NaCl solution. Figure 4b shows the Tafel curves of the different samples. According to the tangent line of the quasi-linear part of the Tafel curve, the corrosion voltage and corrosion current of the samples can be determined. At the same time, the corrosion rate (R_{corr}) can be calculated using the following formula [40,41]:

$$\text{Corrosion Rate} = \frac{I_{\text{corr}} \times K \times EW}{\rho A} \quad (1)$$

where the corrosion rate constant $K = 3272 \text{ mm/yr}$ and the density of Cu substrate $\rho = 8.94 \text{ g/cm}^3$. Since Cu loses 2 electrons due to oxidation, EW is 31.7 g and A is the test area (1 cm^2) of the sample during the test.

As shown in Figure 4b, the bare copper sample showed the maximum corrosion current and the most negative corrosion voltage, indicating that it was the most susceptible to corrosion. With the modification of different 2D films on Cu surfaces, the corrosion current decreased and the corrosion voltage moved in the positive voltage direction, indicating that the samples had stronger corrosion resistance. Compared with the simple growth of a layer of BCN film, further transferring a layer of 2D material on its surface significantly reduced its corrosion current and increased its corrosion voltage, reflecting promotion of the corrosion resistance of 2D materials through grain boundary dislocation. Meanwhile, the in-situ grown BCN/Gr 2D composite film showed a smaller corrosion current and the corrosion voltage moved approximately 15 mV in the positive voltage direction compared with the transferred sample, showing a stronger corrosion resistance ability.

Figure 4c shows the Nyquist diagram obtained by electrochemical impedance spectroscopy (EIS). Within the frequency range of 1–100 kHz, the measured diameter of the half arc could be considered as the interface of charge transfer resistance, representing the corrosion resistance of the protective coating. It can be seen from Figure 4c that the bare Cu substrate showed the minimum impedance, that is, the worst corrosion resistance. With surface modification, the impedance of the sample gradually increased and the BCN/Gr sample showed the strongest corrosion resistance, which was consistent with the results shown in the Tafel curves (Figure 4b). Figure 4d shows the potential dependent EIS results of the in-situ grown BCN/Gr 2D films. The results showed that when the polarization potential changed to the negative direction, the semicircle diameter of the impedance curve increased significantly, indicating that the interface charge transfer resistance increased and had a cathodic protection effect under negative potential. Figure 4e shows the corrosion rates of different samples calculated according to the above formula. The BCN/Gr sample

showed the lowest corrosion rate, that is, the best corrosion resistance. Compared with the bare Cu substrate, the corrosion rate of the BCN 2D material decreased from 0.35 to 0.14 mil/year, with a decrease of 60%. When another layer of BCN or graphene 2D film was transferred on the surface of the in-situ grown BCN 2D film, the corrosion rate was further reduced to 0.08 and 0.07 mil/year, which was nearly 50% lower than that of the single-layer modification. This result proved that the grain boundary dislocation of 2D materials improved corrosion resistance. Furthermore, the corrosion rate of the in-situ grown BCN/Gr 2D composite films further decreased to 0.03 mil/year, which was 91.4% lower than that of bare Cu foil and 57.1% lower than that of the BCN-Gr composite prepared using the transfer method. The further improvement of the anti-corrosion performance of the in-situ grown 2D composite may be due to the dislocation of the grain boundaries of the BCN and graphene layers. In addition, compared with the BCN-Gr two-dimensional composite film obtained by transfer, the interlayer gap of the in-situ grown composite might be smaller, which is more conducive to metal surface protection.

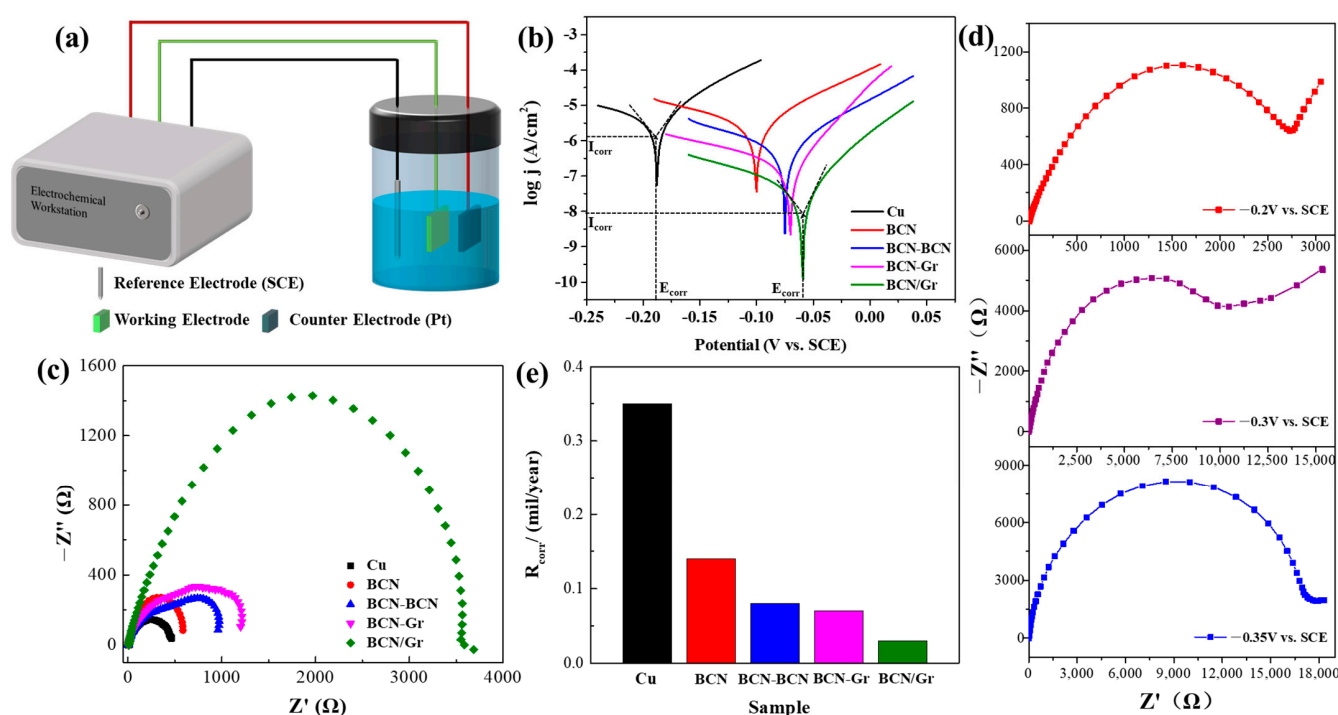


Figure 4. (a) Schematic diagram of the three-electrode system for electrochemical testing; (b) Tafel curves of the Cu foils with different modification layers; (c) Nyquist diagram obtained by electrochemical impedance spectroscopy of the different samples; (d) potential dependent EIS results of in-situ grown BCN/Gr 2D films; (e) Corrosion rates of the samples with different surface modification.

Salt spray testing mainly uses artificial simulated salt spray conditions to assess corrosion resistance ability. In the salt spray experiments, we cut bare copper sheet samples and samples with different surface modifications into 2 cm × 2 cm pieces and placed them into the salt spray box for salt spray testing. After 8 h of spray, the samples were removed and washed with deionized water, and their morphologies were observed after drying. Figure 5a–e shows the optical photos of bare copper foil, BCN, BCN-BCN, BCN-Gr, and BCN/Gr samples after salt spray testing for 8 h. It can be seen that the bare copper foil is most corroded, followed by the sample with a layer of BCN film. After another layer of 2D film was transferred on the surface of BCN, the corrosion was alleviated, and the in-situ grown BCN/Gr sample showed the best corrosion resistance ability, which was consistent with the previous electrochemical test results. Figure 5f–h shows the SEM images of BCN, BCN-Gr, and in-situ grown BCN/Gr samples after salt spray testing for 8 h. It can be clearly seen that the BCN layer grown on the Cu substrate (Figure 5f) was

severely cracked and peeled off from the substrate. At the initial stage of corrosion, the BCN film on the substrate surface could block the corrosion reaction from the Cu foil substrate, thus reducing corrosion. With the extension of time, Cl^- in the corrosive solution gradually passed through the protective layer, and a large amount of Cl^- was adsorbed on the surface of the matrix and reacted with Cu; thus, the BCN film started to be damaged and its anti-corrosion effect was greatly reduced, causing corrosion on the surface of the Cu substrate. As shown in Figure 5g, the BCN-Gr composite prepared by the transfer method had less corrosion and the decorative films were partially complete after the salt spray experiments. The transfer boundary was clear, only small pitting corrosion occurred, and a small amount of salt particles remained. Because of the grain boundary dislocation of the two-layer structure, even the surface layer (graphene) cracked and it was difficult for Cl^- to continue to diffuse through the bottom layer (BCN), causing damage to the Cu substrate. Finally, the in-situ grown BCN/Gr composite showed the best protection effect (Figure 5h). The corrosion mainly occurred at the grain boundary, and other locations were effectively protected except for some residual salt particles. The results of the salt spray experiments were consistent with the electrochemical experiments, confirming the protective effect of the in-situ grown BCN/Gr composite on the metal surface.

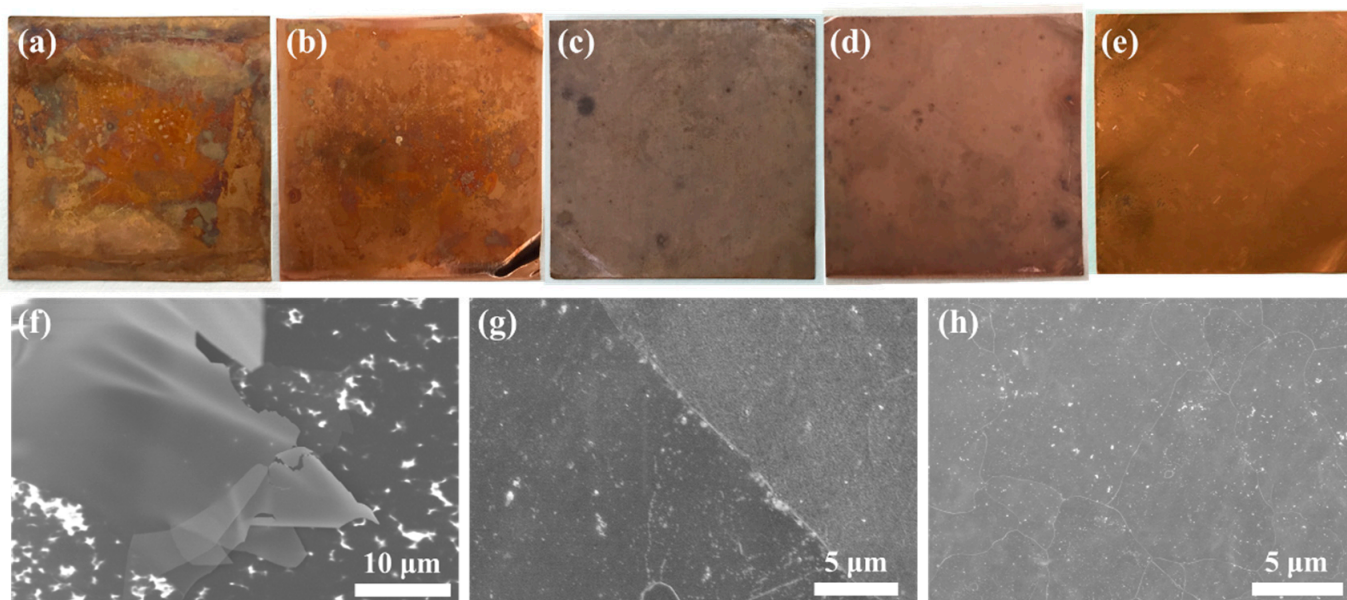


Figure 5. (a–e): Optical photos of bare copper foil (a), BCN (b), BCN-BCN (c), BCN-Gr (d), and BCN/Gr (e) samples after 8 h salt spray testing (sample size: 2 cm × 2 cm); (f–h) SEM images of BCN (f), BCN-Gr (g), and BCN/Gr (h) samples after 8 h salt spray testing.

2D films protect the metal substrate through their tight combination with the substrate and impermeability. Therefore, the combination of the 2D film with the metal substrate is an important factor affecting their anti-corrosion performance. Nano scratch testing is used to characterize the adhesion of 2D materials by testing the force required to peel the 2D film from the substrate [43]. Figure 6a shows the schematic diagram of adhesion test. In this study, a nano indentation instrument was used to evaluate adhesion. By applying 150 μN on the surface of 2D films/copper, nano scratch experiments were conducted, and the curves of transverse force and displacement were obtained (Figure 6b). As shown in Figure 6b, when the indenter peeled the 2D material from the metal substrate surface, significant changes in lateral force can be observed, and the variation in lateral force represents the adhesion between the 2D film and the metal substrate. Figure 6c shows the adhesion of the different samples calculated from the lateral force displacement curve. It can be seen that the BCN film showed the minimum adhesion, which may be related to the larger thickness of the BCN 2D film. After another layer of two-dimensional material

was transferred on the surface of BCN/Cu, the adhesion was increased. The adhesion of BCN-BCN was smaller than that of BCN-Gr, which may be because the BCN film was thicker than the graphene film, thus making it difficult for BCN to closely fit with the substrate. Furthermore, the adhesion of the in-situ grown BCN/Gr composite was significantly higher than that of the composite prepared by the transfer method. This might be attributed to the existence of chemical bonds between the directly grown BCN/Gr layer and the substrate, and the existence of van der Waals forces between the BCN and graphene layers, which shows a closer combination with the substrate. This close combination ensured that corrosive substances were less likely to penetrate into the metal substrate and prevented corrosion reactions.

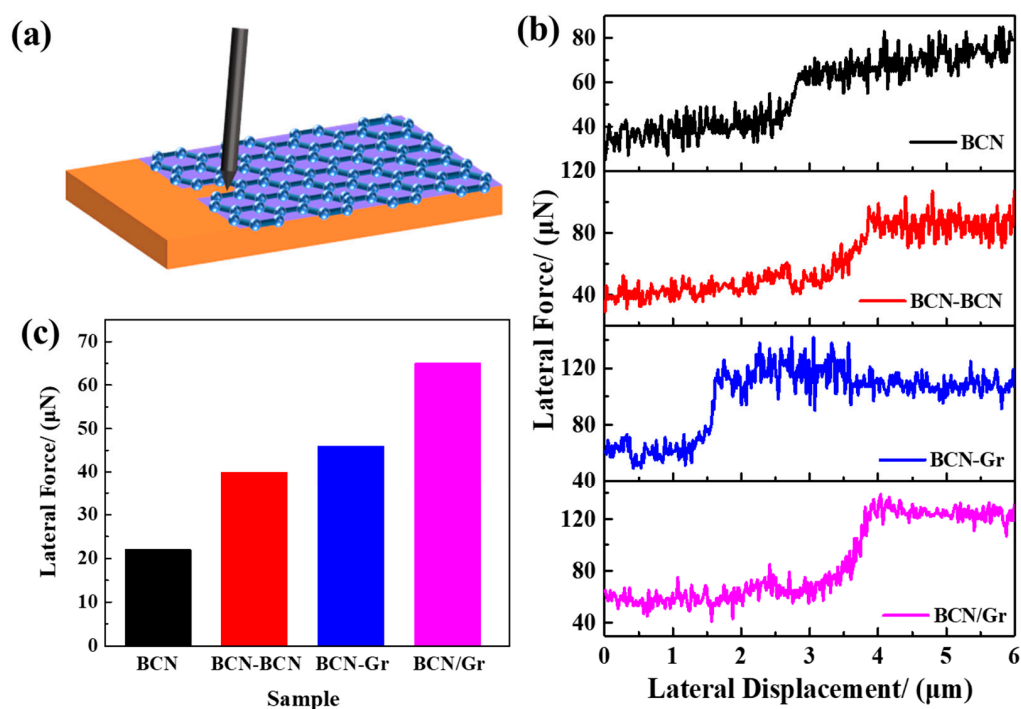


Figure 6. (a) Schematic diagram of adhesion test; (b) The curves of lateral force and displacement of the samples with different surface modifications; (c) Adhesion of different samples calculated from the lateral force-displacement curves.

3. Materials and Methods

3.1. CVD Growth of BCN 2D Films

BCN 2D films were grown using the CVD method, with methane and borane ammonia used as the precursors, Cu foil used as the substrate, and the carbon source flow rate and growth time as the variables. As shown in Figure 1a, the growth process had two heating zones. After exhausting the air in the tubular furnace with Ar, the temperature of the main heating zone was raised to 1000 °C, and the mixed gas of methane and hydrogen was introduced, in which the dehydrogenation of methane molecules produced carbon atoms. Then, the temperature of the auxiliary heating zone was set to 90 °C, and the borane ammonia was decomposed by heat to produce $\text{-BH}_2\text{-NH}_2\text{-}$, which diffused to the main heating zone with the gas flow, decomposed into -B-N- under the high temperature, and was deposited on the copper substrate with carbon atoms to generate the BCN films. The variables in this experiment were carbon source flow rate and growth time, which were $\text{CH}_4 = 20$ sccm, growth for 10 min; $\text{CH}_4 = 40$ sccm, growth for 20 min; and $\text{CH}_4 = 40$ sccm, growth for 40 min. The samples were named BCN1, BCN2, and BCN3, respectively.

3.2. In-Situ Catalytic Growth of BCN/Gr 2D Composite Films

The preparation of BCN/Gr two-dimensional composite films also used the CVD method, which combined the growth processes of graphene and BCN in the same procedure, with copper foil used as the catalyst and borane ammonia and methane as the precursors. First, we used methane as the carbon source to grow graphene two-dimensional films. During the growth process, clean copper sheets were first put into the main heating zone of the CVD furnace. Subsequently, the quartz tube was vacuumed. After the internal pressure of the system was pumped below 30 pa, it was filled with Ar to normal pressure, and vacuumed it again. This process was repeated three to four times until no air existed in the system. Then, Ar was introduced and its flow was adjusted to 100 sccm. After the inert atmosphere in the quartz tube was adjusted, the temperature of the main heating zone was raised to 1040 °C at a heating rate of 14 °C·min⁻¹, and H₂ was introduced. The flow rate was set at 15 sccm and the temperature was maintained for 30 min. Then, methane (20 sccm) was introduced and the carbon atoms were arranged on the surface of the Cu foil for 20 min. After the growth of the graphene layer, the temperature of the main heating zone was reduced to 1000 °C with the flow rates of methane and hydrogen maintained at 40 and 15 sccm, respectively. Then, heating tape was wound around the auxiliary heating zone to keep the temperature at 90 °C for the decomposition of borane ammonia. At 1000 °C, the flow rate of H₂ was 15 sccm, the flow rate of CH₄ was 40 sccm, and the growth time was set at 10, 20, and 40 min to finally realize the preparation of BCN/Gr composite films. The samples were named BCN/Gr1, BCN/Gr2, and BCN/Gr3, respectively. After the growth period was complete, the heating band was removed, the CH₄ and H₂ were turned off, and the sample was cooled in the furnace to room temperature. Then, the system was filled with Ar to normal pressure and the sample was removed.

3.3. Preparation of BCN-BCN and BCN-Gr 2D Composites by Transfer Method

With PMMA as the transfer carrier, the copper substrate under the BCN and graphene films was etched using the chemical etching method, the BCN and graphene films were transferred to the BCN/Cu grown under different conditions, and the PMMA was removed by acetone after drying. The samples that were prepared by transferring a layer of BCN on the basis of the BCN/Cu grown by the CVD method under different conditions were named BCN-BCN1, BCN-BCN2, and BCN-BCN3, respectively. The samples that were prepared by transferring a layer of graphene film on the basis of the BCN/Cu grown by the CVD method under different conditions were named BCN-Gr1, BCN-Gr2, and BCN-Gr3, respectively.

3.4. Electrochemical Test

A three-electrode system was used for electrochemical testing to evaluate the corrosion resistance of the samples. The platinum electrode was used as the counter electrode and the saturated calomel electrode was used as the reference electrode. The test was conducted in 5% NaCl solution. The test sample was sealed with silicone rubber, leaving a 1 cm² exposed area to be measured. After the silicone rubber was completely cured, the samples were used as the working electrode to obtain Tafel curves and electrochemical impedance spectroscopy (EIS) was conducted on the samples in the three-electrode system. The frequency range was set as 1~100 kHz during the EIS tests. Finally, the corrosion rates were calculated by determining the tangent lines of the Tafel curves.

3.5. Salt Spray Test

A salt spray box was used for salt spray testing. First, 5% NaCl solution was prepared and the pH value was adjusted to 6.5–7.2. Then, the samples to be tested were put into the salt spray box and the samples were inclined at an angle of 15–30° to the vertical plane. After spraying for 8 h, the samples were removed, and the salt particles attached to the surface were quickly washed with deionized water. Finally, further characterizations were carried out after the samples were dried.

3.6. Nano Scratch Test

A Hysitron TriboScope nano indenter was used to conduct the nano scratch experiments. The indenter used in the experiment was a Berkovich diamond indenter and the curvature radius of the tip was approximately 150 nm. A transverse force (150 μ N) was applied on the two-dimensional film/Cu substrates, and the nano scratch experiments were carried out to obtain the curves of transverse force and displacement. When the indenter peeled the two-dimensional material from the substrate surface, significant changes in the lateral force were observed. The difference between the lateral force was identified as the adhesion between the material and the substrate.

4. Conclusions

In conclusion, BCN/Gr 2D composite with a complete structure was directly grown on the surface of copper foil by in-situ catalytic growth and delicately controlled precursors and reaction conditions. Through morphological analysis, electrochemical testing, adhesion measurements, and salt spray testing, it can be seen that the in-situ grown BCN/Gr 2D composite exhibited the best anti-corrosion ability with the advantages of grain boundary dislocation and strong adhesion with the metal substrate. As a result, the corrosion resistance of the in-situ grown BCN/Gr composite was greatly improved, with a corrosion rate 91.4% and 57.1% lower than that of bare Cu foil and BCN-Gr composite prepared by the transfer method, respectively, showing its potential in corrosion protection applications. This study not only proposes a new strategy for preparing new 2D composite films, but also provides a new approach for the application of 2D nanomaterials in corrosion protection.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12121618/s1>, Figure S1: SEM image of graphene grown on Cu foil; Figure S2: EDS of BCN/Gr 2D composite film; Figure S3: (a) TEM and (b) AFM of in-situ grown BCN film; (c) TEM and (d) AFM of BCN/Gr 2D composite film; Figure S4: Diagram of liquid etching method and preparation of BCN-BCN and BCN-Gr samples; Figure S5: Raman spectrum of CVD grown graphene.

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