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The synthesis of graphene coated copper from PMMA and the anticorrosion performance of copper substrate

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Abstract

In this research, the low temperature process for growing graphene from solid carbon source PMMA under atmospheric pressure was firstly investigated. Through adjusting the growth temperature (600 °C–800 °C) and other process parameters, using the chemical vapor deposition method, single or double layers of graphene grown on a copper substrate. Without control pressure, this way improved controllability of graphene preparation and reduced production costs. The morphology, quality of graphene was revealed by SEM, XPS, Raman, UV−vis. Additionally, the conductive test results illustrate that the graphene on the surface of the copper matrix slightly soars the conductivity of copper. This is due to the process of annealing and growth that alters the structure of the material. The results of the Tafel experiments, electrochemical impedance spectroscopy (EIS) measurements and cyclic voltammetry (CV) tests demonstrate that the graphene film can effectively improve the corrosion resistance of the copper matrix. Compared to the single layer graphene coating, double-layers graphene coating has a better anti-corrosion effect. This is in that the double-layers graphene coating can block the defects of the single-layer graphene in time, and better prevent the intrusion of Cl − into the copper matrix, so as to achieve a good anti-corrosion effect.

1. Introduction

Graphene, a novel two—dimensional material (single—layer graphene thickness is 0.335 nm), is a hexagonal lattice planar film composed of a single layer of carbon atoms in a SP2 hybrid connection [1−3]. The unique physical and chemical properties of graphene, such as ultra—thin geometry, chemical inertness, thermal and chemical stability, mechanical strength and impermeability to ion diffusion [4−7], make it widely used in the field of anti-corrosion [8, 9], energy storage [10, 11], optical materials [12, 13], abrasion-resistant composite materials [14], high-strength composite materials [15] etc.

In recent years, high-quality, large-area graphene has been prepared by chemical exfoliation, mechanical exfoliation, chemical synthesis, chemical vapor deposition (CVD), in which CVD is used to prepare high-quality graphene state on a metal substrate by catalyzing the gaseous, solid carbon precursors, etc, improve the controllability of graphene, the most widely used [16, 17]. The choice of carbon source is the key to CVD technology. PMMA has been widely studied and used because of its low C—H bond energy, which reduces the growth temperature and saves production costs. Sun [18] et al used PMMA as a carbon source to prepare high-quality graphene at temperatures as low as 800 °C. Li [19] et al have conducted in-depth research to prepare graphene at a temperature of at least 400 °C. However, their experiments were also completed under high pressure conditions. This harsh condition is not conducive to its large-scale production, and further research is needed.
Copper and its alloys have been widely used in ground transportation, aerospace, military, marine and other fields for their excellent machinability and high thermal and electrical ductility [20–22]. However, the corrosion loss of copper and its alloys has been a problem that has plagued. In response to this issue, scientists have been working to improve their corrosion resistance [23–25]. In recent years, the application of nanocomposite coatings, hydrophobic coatings and organic-inorganic hybrid coatings has significantly improved the service life of copper and its alloy materials, released significant economic costs [26, 27]. However, due to the thickness of coatings, existing coating techniques typically modify the physical properties of the copper matrix, such as physical dimensions, appearance and optical properties, and reduce electrical conductivity. The research of ultra—thin anti—corrosion coatings can overcome these shortcomings and almost keep the physical and chemical properties of the metal substrate [28]. The in situ synthesis of graphene ultrathin coating on a copper substrate by chemical vapor deposition can improve the corrosion resistance of the copper matrix and provide the service life of the copper—based material. Studies have depicted that structural characteristics such as the number of layers of graphene have a great influence on the corrosion resistance [29]. The process of low temperature and atmospheric pressure growth on the copper matrix can reduce the growth conditions of graphene, provide the possibility of large-scale production, and lay a foundation for the anti—corrosion direction of copper—based materials, which is particularly important.

This experiment confirms that the graphene film derived from the solid carbon source PMMA can effectively protect the copper matrix and improve its corrosion performance in high concentration NaCl solution. For the first time, the solid carbon source PMMA was used to investigate the growth process of graphene on a copper substrate under atmospheric pressure and low temperature. Through the modified tube furnace, the carbon source and the copper matrix were heated in the independent respectively temperature zones, and the process parameters such as growth time and growth temperature are reasonably regulated, and the controllable growth of the single—layer and double—layers graphene film on the copper substrate is realized without controlling the low pressure. In the case of a slight increase in the conductivity of the different layers of graphene coated copper materials, which were further studied by the potentiodynamic polarization experiment, EIS measurements and CV tests, acted as an anti—corrosion coating to quantify the degree of corrosion inhibition of the coating. The experimental results represent that the graphene film can improve the inhibition ability of the copper matrix in the cathodic reduction reaction during the electrochemical reaction, thereby preventing the intrusion of Cl$^-$ into the copper matrix. Double—layers graphene can effectively block the defects of single—layer graphene and exhibit better corrosion resistance. It has excellent application in the anti—corrosion direction of copper and its alloys.

2. Experimental details

2.1. Preparation of graphene—coated Cu samples.
The modified tubular furnace (OTF—1200X, Hefei Kejing) was used to prepare the graphene coated Cu samples. First, the solid feedstocks PMMA contained in the minor quartz boat was placed on the gas inlet side of the quartz tube, just outside the heating zone. The device diagram is shown in figure 1. Then, the 35 μm thick Cu foils (Alfa Aesar) were heated to 800 °C in a 100 sccm H$_2$ streams and a 4000 sccm Ar streams, annealed for 45 min, cooled to room temperature, and raised to the desired growth temperature (800 °C, 700 °C, 600 °C). The carbon precursor was heated by a heating tape wound on a quartz tube (heating temperature is about 160 °C), the H$_2$ flow rate is kept constant, and growth is carried out for several minutes at a certain growth temperature. Last, the furnace is turned on for rapid cooling. The grown graphene film was transferred to a Si substrate having a 300 nm thick oxide coating layer by PMMA wet transfer method for corresponding characterization.

2.2. Characterization
Scanning electron microscopy (SEM, FEI Quanta 450) was used to observe the surface morphology of graphene, x—ray photoelectron spectroscopy (Thermo ESCALAB 250) was used to characterize the SP$^2$ degree of graphene, and the Raman probe spectrometer (HORIBA Labram HR ELECTION) was used to characterize the layers and defect, ultraviolet spectrophotometer (JASCO—V570) was used to characterize the transmittance of graphene.
A polarization test was performed on the corrosion potential under the condition of a scan rate of 0.1 mV s\(^{-1}\) less than 10 mV were considered to be stable potentials prior to the corrosion test. The potentiostatic circuit potential was monitored for 2 h to determine its stability. Any electrode the remainder is embedded in the epoxy resin, placed in the vertical pressure direction and the reference electrode (saturated calomel electrode (SCE)). All experiments were performed at room temperature. The open circuit potential was monitored for 2 h to determine its stability. Any fluctuations in the open circuit potential of less than 10 mV were considered to be stable potentials prior to the corrosion test. The potentiostatic polarization test was performed on the corrosion potential under the condition of a scan rate of 0.1 mV s\(^{-1}\) within \(\pm 300\) mV of the OCP. Corrosion potential (\(E_{\text{Cor}}\)) and corrosion current density (\(I_{\text{Cor}}\)) were determined on the driven potential polarization curve. The sample was measured at a frequency range of \(10^{-2}\)–\(10^{5}\) Hz and a sine wave vibration amplitude of 20 mV to obtain an EIS result. In addition, EIS data was fitted by an equivalent Randles circuit to obtain detailed information about sample corrosion. The potential range of the CV test was set to a linear sweep of \(-0.2\) V (SCE) to \(-0.7\) V (SCE) at a scan rate of 10 mV s\(^{-1}\).

### 2.3. Corrosion tests

Electrochemical measurement of an electrochemical workstation (CHI—660E) equipped with a conventional three—electrode system in a 3.5 wt% NaCl solution, the system comprising a counter electrode (with a 2.5 cm\(^2\) area of platinum plate) and a working electrode (2.25 cm\(^2\) exposure). The area of the graphene coated Cu sample, the remainder is embedded in the epoxy resin, placed in the vertical pressure direction and the reference electrode (saturated calomel electrode (SCE)). All experiments were performed at room temperature. The open circuit potential was monitored for 2 h to determine its stability. Any fluctuations in the open circuit potential of less than 10 mV were considered to be stable potentials prior to the corrosion test. The potentiostatic polarization test was performed on the corrosion potential under the condition of a scan rate of 0.1 mV s\(^{-1}\) within \(\pm 300\) mV of the OCP. Corrosion potential (\(E_{\text{Cor}}\)) and corrosion current density (\(I_{\text{Cor}}\)) were determined on the driven potential polarization curve. The sample was measured at a frequency range of \(10^{-2}\)–\(10^{5}\) Hz and a sine wave vibration amplitude of 20 mV to obtain an EIS result. In addition, EIS data was fitted by an equivalent Randles circuit to obtain detailed information about sample corrosion. The potential range of the CV test was set to a linear sweep of \(-0.2\) V (SCE) to \(-0.7\) V (SCE) at a scan rate of 10 mV s\(^{-1}\).

### 3. Results and discussion

#### 3.1. Characterization of graphene

Figure 2(a) shows a commercially available solid carbon source powder. As a solid carbon source, polymethyl methacrylate (PMMA) has a weaker C–H bond energy (283–288 KJ mol\(^{-1}\)) to CH\(_4\) (410 KJ mol\(^{-1}\)). Typical gas carbon precursors such as C\(_2\)H\(_2\) (443 KJ mol\(^{-1}\)) and C\(_2\)H\(_4\) (506 KJ mol\(^{-1}\)) are weak and have relatively low energy barriers during decomposition, which can be used in the process of preparing graphene by CVD under low temperature conditions [30, 31]. Figure 2(b) shows the Raman spectrum of PMMA. PMMA provides carbon precursors about graphene growth, which can significantly affect the growth of graphene during CVD. The peak at 601.2 cm\(^{-1}\) is generated by the stretching vibration of the 8 C–1 C–3 O bond; the stretching vibration of the 1 C–3 O–4 C bond corresponds to the peak at 814.1 cm\(^{-1}\); 3 O–4 C (5 H, 6 H, 7 H) In-plane rocking vibration mode corresponds to the peak at 988.2 cm\(^{-1}\); 9 C–(10 H, 11 H) –deformation vibration and 3 O–4 C (5 H, 6 H, 7 H) symmetrical deformation bending vibration corresponds to, 1452.7 cm\(^{-1}\), the peak of the place [32]. The presence of different hydrocarbons in the PMMA molecule has a good synergistic effect on the formation of graphene.

Figure 3 shows an SEM picture of single crystal graphene and its aggregation to form a graphene film under different process conditions. Figures 3(a), (b) shows an image of graphene grown under process conditions at a growth temperature of 800 °C. As can be seen from figures 3(a), (b), by controlling the CVD reaction time, a single crystal graphene island and its aggregate structure were obtained. Figure 3(a) shows a clear view of the graphene structure of different shapes and orientations on copper grains. This image shows the hexagonal sharp edges of graphene crystals, which are the basis for large-area continuous films. The growth of graphene across the Cu twin boundary was also observed. The shape of the graphene crystal is not affected by the grain boundaries for the reason that the hexagonal shape across the Cu grains and grain boundaries remains unaffected. With PMMA as the carbon source, a growth of graphene islands of uniform size of about 2 \(\mu\)m was observed on the copper foil. This is due to the pretreatment of the copper foil (including electrochemical...
polishing and thermal annealing) to provide a uniform growth substrate with a crystal plane [33, 34]. As the growth time prolongs, the individual graphene crystals crosslink each other and combine to form a continuous film. On the surface of the substrate, fine wrinkles can be observed (figure (b)). This is due to the difference in the expansion coefficient between the graphene and the copper matrix, resulting in wrinkles in the graphene [35]. Figures 3(c), (d) shows the microscopic morphology of the sample at a growth temperature of 700, 600 °C. At the growth temperature of 700 °C, significant wrinkles were observed. The wrinkles become thicker than the growth conditions of 800 °C, which indicates an increase in the number of graphene layers. Under the growth conditions of 600 °C, the carbon deposits on the surface of the sample increase, which is caused by the excessive carbon atoms at low temperature and cannot be converted into graphene film, which also indicates the significant enhancement of graphene defects.

X-ray photoelectron spectroscopy was performed on graphene coated Cu samples prepared at different growth temperatures. Figure 4(a) shows the broad XPS spectra of graphene films deposited on copper foil at different temperatures. The broad XPS spectrum clearly shows a C1s peak at about 284.5 eV, an O1s peak at about 531 eV, a Cu LMM peak at about 570 eV, a Cu 2p3/2 peak near 932 eV, and a Cu 2p1/2 peak at about 951.2 eV. The presence of oxygen is caused by the migration of oxygen dissolved in the interior of the copper foil to the surface during growth, and the results of the graphene films prepared under different conditions are almost the same [36]. Figures 4(b)–(d) show the XPS spectra of the photoelectron—emitting graphene film of the C1S nuclear level peak under different growth conditions (800 °C, 700 °C, 600 °C), the peak consisting of two components, The carbon bond group is hybridized by SP3 at a binding energy of 284.5 eV, C = C SP2 bond in the graphite network, and another at 285.6 eV. As the growth temperature decreased, the strength of the SP3 component increased significantly (from 10.1% to 19.5%), indicating that the carbon deposit on the surface increased significantly. This transformation is caused by a decrease in growth temperature, where excessive carbon atoms are not concentrated on the surface of the copper foil, which is consistent with the SEM observation.

Figure 5(a) shows the Raman spectra at various growth temperatures. In order to verify of the graphene layers number, defects, etc, the graphene coated Cu samples prepared at different growth times were transferred to the surface of the SiO2/Si substrate, and Raman spectroscopy was performed. The two most essential characteristic peaks, the G and 2D peaks, are located near 1580 cm⁻¹ and 2690 cm⁻¹, the weaker D peak is located near 1350 cm⁻¹, and the double degenerate phonon mode at the center of the G and Brillouin zones (The transverse optical branch is closed to the longitudinal optical branch and has E2g symmetry. The D peak and the 2D peak are generated by the second-order double resonance Raman scattering process in the first Brillouin zone, wherein the 2D peak originates from the in-plane transverse optics at the boundary of the region. The phonon is derived, and the D peak originates from the phonon branch near the K point in the structure and
requires a defect to activate [37, 38]. It can be seen from figure 5(a) that the typical characteristics of single-layer graphene are shown at a growth temperature of 800 °C: the 2D band centered on \( \sim 2692 \text{ cm}^{-1} \) is symmetrical, exhibiting a perfect Lorentz peak type. G peak and 2D peak, the intensity ratio of \( \frac{I_{2D}}{I_G} \) is \( \sim 1.51 \). The D-band \( \sim 1352.8 \text{ cm}^{-1} \), which is representative of graphene defects, demonstrates the high quality of graphene. Under the growth conditions of 700 °C, although the graphene characteristics (G, 2D peak) can be exhibited, the half width of the 2D peak increases, and the intensity ratio of the G peak to the 2D peak \( \frac{I_{2D}}{I_G} \) is \( \sim 1.1 \), showing the characteristics of double-layer graphene. Under the growth conditions of 600 °C, compared with the growth
conditions of 700 °C, the D peak of the graphene defect is predicted to be enhanced, but the intensity ratio of the G peak to the 2D peak ($I_{2D}/I_G$) is $\sim 0.9$, and the Characteristics of double-layers graphene is still exhibited. This is due to the decrease in growth temperature, many surface carbon atoms have not yet come and are converted into graphene films under the action of hydrogen. They are agglomerated with carbon-containing molecules transported with high argon to form carbon deposits, resulting in obvious defect and the apparent increase in the D peak.

The transmittance of the sample at a laser intensity of 550 nm was measured using an ultraviolet spectrophotometer. Graphene has excellent light transmission properties, and theoretically, the transmittance of single-layer graphene can exceed 97.7%. It is almost completely transparent in the visible light region, but as its number of layers increases, its light transmittance tends to decrease [39]. In general, the transmittance of graphene is related to its thickness, and is also affected by the uniformity of graphene and the degree of defects. The results of the light transmittance test are shown in figure 5(b). The samples having growth temperatures of 600 °C, 700 °C, and 800 °C, respectively, had light transmittances of 93.1%, 94.4%, and 97.3%, respectively. A single-layer graphene film was formed on the surface of the copper foil at a growth temperature of 800 °C, and a double-layers graphene film was formed at 600 °C and a temperature of 700 °C. However, the surface has defects at 600 °C, and the light transmittance can only reach 93.1%. This is because the growth temperature is too low, the carbon deposit on the surface increases, and the transmittance decreases significantly, which is consistent with the Raman spectrum.

3.2. Conductive performance

Pure copper, single-layer graphene coated copper (800 °C growth conditions, SLG/Cu), double-layers graphene coated copper (700 °C growth conditions, BLG/Cu) were used to test the electrical conductivity. Figure 6 shows the U–I curve obtained by isometric testing of a four-probe resistance tester. It can be seen from the slope of the curve that the conductivity of the sample is slightly increased after the growth of the graphene, but within the
precision range of the instrument, the number of layers of the surface graphene has little effect on it. The results show that the graphene coating does not reduce the conductivity of copper, but increases slightly. This is because the high temperature annealing of the copper foil substrate causes the grain to become larger, the grain boundary is reduced, and the conductivity is slightly increased. In addition, the carbon doping of the carbon source causes a change in the surface structure of the copper substrate, which also causes a slight increase in conductivity.

3.3. Corrosion behavior

Pure copper, SLG/Cu, BLG/Cu samples were used to test the corrosion resistance. Figure 7(a) shows the OCP of bare copper and graphene coated Cu samples in a 3.5 wt% NaCl solution at room temperature. The OCP of SLG/Cu (−149 mV) and BLG/Cu (−142 mV) is higher than that of pure Cu (−154 mV). Significant changes in OCP indicate that GR/Cu has high corrosion resistance. In order to further determine the corrosion behavior, the Potentiodynamic polarization curves and corrosion patterns were studied.

Figure 7(b) shows the potentiodynamic polarization curves of pure Cu and SLG/Cu and BLG/Cu samples in a 3.5 wt% NaCl solution at room temperature. Corrosion data are shown in Table 1. Since the corrosion of copper corrosion is proportional to the concentration of chlorine (Cl) ions contacting the metal surface, a 3.5% sodium chloride concentration (corresponding to 0.6 M NaCl) is selected as the etching solution condition. The corrosion process of the Cu sample consists of an anodic oxidation reaction (Cu → Cu^{2+} + 2e^{-}) and a cathodic reaction (O_{2} + 2H_{2}O + 4e^{-} → 4OH^{-}, oxygen reduction). The polarization curves of SLG/Cu and BLG/Cu samples show a significant positive change in corrosion potential (325.2 mV, 251.8 mV) compared to bare copper (418.9 mV). Confirming the graphene coated Cu samples has better corrosion resistance than Bare copper. The anti-corrosion efficiency of the graphene coated Cu samples can be calculated as follows:

$$\eta = \frac{ICu - IGR/Cu}{ICu} \times 100\%$$

Where I is the polarization current density. The inhibition efficiency of SLG/Cu and BLG/Cu samples was calculated to be 65.16% and 77.73%. The corrosion rate (CR) is estimated from the corrosion current value using the standard formula (equation (2)) described in ASTM Standard G102 [40]:

$$CR = K [icorr/\rho A] \times EW$$

Among them, the corrosion constant K = 3.272 mm yr^{-1}, the equivalent weight EW = 31.7 g Cu, the Cu density = 8.97 g cm^{-3}, A = 2.25 cm² sample area. The CR of Cu, SLG/Cu and BLG/Cu composites were calculated to be 2.489 mm yr^{-1}, 0.867 mm yr^{-1}, and 0.554 mm yr^{-1}, respectively.

In order to further study the corrosion mechanism of the graphene coated Cu samples, we obtained the SEM image and EDS image of the corrosion sample. Figure 8(a) clearly shows that the pure Cu surface is completely damaged and has many defects, resulting in dissolution of Cu. The EDS pattern of the indicated region indicates the presence of Cl⁻ on the surface of pure Cu. The peak of Cl⁻ also reflects that the pure Cu surface is covered with a large amount of corrosion products. It can be seen from the figure 8(a) that the infiltration of the attracted

| Surface   | OCP (mV) | Ecorr (mV) | Icorr (uA cm^{-2}) | CR, mm/year | PE, %  |
|-----------|----------|------------|--------------------|-------------|--------|
| Bare copper | -154     | 418.9      | 21.54             | 2.489       | —      |
| SLG/Cu    | -149     | 325.2      | 7.504             | 0.867       | 65.16  |
| BLG/Cu    | -142     | 251.8      | 4.796             | 0.554       | 77.73  |

![Figure 8. SEM Morphology and EDS images after corrosion tests of (a) pure Cu, (b) SLG/Cu, (c) BLG/Cu samples.](image)
occurs as follows: $2Cu^+ + 2Cl^- = 2CuCl, 2CuCl + H_2O = Cu_2O + 2H^+ + 2Cl^-$. However, as shown in figures 8(b), (c), we observed that the concentration of Cl on the surface of the graphene coated copper sample was much lower, and the change in the surface of Cu was not significant except for the trace amount of white salt. Ultimately, the large inhibition of the cathodic layer on the cathodic reaction results in a significant decrease in $I_{corr}$ and a significant reduction in the $E_{corr}$ of the graphene coated Cu samples. Compared to SLG/Cu sample, the BLG/Cu sample has fewer corrosion areas and better corrosion protection.

Figure 9 shows the EIS test results of pure Cu and SLG/Cu and BLG/Cu materials, including Nyquist plots ($Z$ and $Z_{real}$, figure (a), Bode plots ($|Z|$ and $log\omega$) plot (b), inset is an analog equivalent circuit diagram). Electrochemical impedance spectroscopy (EIS) of electrochemical technology can be used to represent the electrochemical corrosion reaction of the interface coating between the electroactive ion species and the metal surface. Its core is to distinguish the different speed processes in the electrochemical reaction process by the change of frequency. Nyquist and Bode diagrams are the most common representations of various interface reactions [41]. In figure 9(a), the abscissa of the first point in the high frequency domain represents the equivalent series resistance of the capacitor. The smaller the abscissa value, the smaller the electrode resistance, and the more favorable the electron transfer within the electrode [42]. It can be seen that the presence of graphene reduces the internal resistance and the resistance of the surface electrodes. This is consistent with the conductivity data of the material measured by the U-I curve. In figure 9(b), the modulus in the low frequency region characterizes the corrosion resistance of the material. The higher the modulus value in the low frequency region, the stronger the corrosion resistance of the material. It can be concluded that the graphene coating reduces the possibility of dissolved oxygen, water, and chloride ions penetrating the Cu surface, and increases the corrosion resistance. Compared to single-layer graphene, double-layer graphene can effectively block related ions. When it reaches the surface of the copper substrate, the corrosion resistance is better. This is consistent with the results measured by the Tafel polarization curve.

Figure 10 shows the CV curves of pure Cu and SLG/Cu and BLG/Cu materials in 3.5% NaCl solution. The shapes and structures of different peaks are shown in the figure. The cyclic voltammetry process of the Cu sample consists of an anodic oxidation reaction ($Cu-e^-\rightarrow Cu^+, Cu^+-e^-\rightarrow Cu^{2+}$) and a cathodic reaction ($Cu^{2+} + e^-\rightarrow Cu^{+}, Cu^{+} + e^-\rightarrow Cu$). For pure copper materials, the main component in the solution is copper and its oxides. The formation of the first oxidation peak is related to Cu or Cu$_2$O, and the formation of the second oxidation peak is related to CuO or Cu(OH)$_2$. During the reverse scanning process, the reduction peak is Cu$^{2+}$ or Cu$^+$ through complex reduction reactions to generate Copper Elemental formation. In the first scan, the oxidation reaction is suppressed. In the second and subsequent scans, the anode and cathode peaks gradually increased. This indicates that corrosion occurred on the surface of the copper substrate [43, 44]. For the SLG/Cu material, we observed that the curve is somewhat similar to that of the pure copper sample, which indicates that a redox reaction occurred in the uncovered part of graphene. In five consecutive scans, we found that Compared with pure copper samples, oxidation, reduction current is decreased, and the degree of oxidation reduction is reduced. For the curve of BLG/Cu material, we can see that the peak current of the oxidation peak and reduction peak is significantly reduced, and the oxidation-reduction reaction is almost suppressed. This means that the presence of the graphene layer can reduce the redox reaction of the copper substrate in the NaCl...
solution, thereby reducing the corrosion rate of the copper substrate and providing a good protection for the copper substrate. Compared with single-layer graphene, the double-layer graphene layer has a higher surface coverage of the copper substrate, a better barrier effect, and a better anti-corrosion effect.

As figure 11 shown is, the reason is that the graphene coating prevents the infiltration of corrosive chloride ions into the underlying metal. Because the graphene coated copper material has a much lower affinity for oxygen reduction, there is a corrosion barrier between the aggressive Cl ions in the solution and the Cu surface, shielding the ion migration between the copper matrix and the NaCl electrolyte, blocking the transport path of ions in the solution reduces the reaction power of the formula: \( \text{Cu} \rightarrow \text{Cu}^{2+} + 2e^- \), which greatly improves the corrosion resistance of copper. The reason why the double-layers graphene coating has better corrosion resistance is that the in situ synthesis of graphene is completed by depositing and assembling carbon atoms on the surface of the copper substrate. Due to the structural difference of the carbon precursor, the quality defect of the surface of the copper substrate and the randomness of the deposition causes vacancy defects in the graphene, etc, and it is impossible to prepare a two-dimensional crystal which is uniform and defect-free on a large scale. Compared with single-layer graphene coating, the double-layers graphene coating can cover the defects of single-layer graphene during CVD in situ growth, and prevent \( \text{Cl}^- \) and other immersion into copper matrix to achieve better corrosion performance.

4. Conclusion

Graphene coated Cu material derived from PMMA was firstly prepared at different growth temperatures by double-temperature zones heating under atmospheric conditions, which was demonstrated good corrosion resistance in a 3.5% NaCl environment. The carbon source and copper matrix are heated in the double temperature zones to realize in situ synthesis of controllable layer graphene at different growth temperatures,
which is realized by using the modified tubular furnace. Due to the unique structure of graphene, it exhibits good barrier properties (Corrosion resistance rate is 3 times higher than bare copper) and prevents chloride from diffusing into the copper matrix in a NaCl environment. The double-layers graphene exhibits superior barrier properties because the double-layered graphene can effectively block the defects of the single-layer graphene and more effectively block the diffusion of chloride into the copper matrix. In short, a controllable graphene layer was synthesized by in situ synthesis to enhance the corrosion resistance of the copper matrix. This convenient and simple graphene preparation method can realize the quantitative control of the coating, and has great application prospect in the corrosion resistance direction of copper and its alloy.

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Conflict of interest

The authors declare no conflict of interest.

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