

Article

Long-Term Corrosion Protection of a Cupro-Nickel Alloy Due to Graphene Coating

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Abstract: This study demonstrates the corrosion resistance of a Cu-Ni alloy coated with a multi-layer graphene. This is one of the first demonstrations of long-term corrosion resistance due to graphene coating, which is crucial since earlier studies have suggested graphene-coated copper to be considerably inferior to bare copper in terms of corrosion during long-term exposure to a corrosive environment. The inferior corrosion resistance of graphene-coated copper arises due to defects and poor surface coverage by graphene. Since it is prohibitively difficult to develop defect-free graphene on metals at a commercially feasible scale, this study investigated the hypothesis for an alternative approach, i.e., to develop multi-layer graphene with a reasonable assumption that the areas of defects/poor coverage of a layer will be masked by the subsequent over-layer(s). This study has validated this hypothesis. Electrochemical investigations have demonstrated multi-layer graphene to improve the corrosion resistance of a Cu-Ni alloy by an order of magnitude. However, the most striking finding of this study is that the improvement in corrosion resistance due to the multi-layer graphene coating sustained the entire duration of a long-term test (~350 h).

Keywords: Cu-Ni alloy; graphene; EIS; Raman spectroscopy; chemical vapour deposition; corrosion

1. Introduction

Corrosion and its mitigation are an ongoing and costly problem [1]. Therefore, successful application of a novel approach to mitigation of corrosion has attractive socioeconomic implications. An ultra-thin barrier coating of graphene is a disruptive approach to corrosion resistance. The great interest in graphene as an effective coating for corrosion resistance arose due to highly relevant properties of graphene, such as remarkable chemical inertness (even to aggressive HF) [2], impermeability (even to tiny He atom) [3], and high toughness [4]. Politano and Chiarello [5] demonstrated that the Poisson's ratio and 2D Young's modulus of graphene were 0.19 and 342 N/m, respectively, in the case of both flat and corrugated graphene, showing the usefulness of graphene for electromechanical devices and carbon-fibre reinforcements. There have been a few studies showing water adsorption on graphene [6,7]; however, this does not contradict the idea that graphene is chemically inert, for adsorption is not a chemical reaction. The growth of graphene on bimetallic surfaces such as Pt₃Ni (111) is another area of recent interest since graphene provides enhanced catalytic activity to such surfaces [8]. Furthermore, graphene-based membranes have attracted interest for desalination as well as liquid and gas separation [9]. Corrosion resistance of an ultra-thin graphene-coated copper was found to be superior to bare copper by up to two orders of magnitude in an aggressive chloride solution (similar to seawater) [10]. Chen et al. [11] were the first to investigate the ability of graphene coating to provide corrosion resistance.

They grew a monolayer of graphene on top of Cu and a Cu/Ni alloy using an established CVD process. They demonstrated that graphene coating could effectively protect the surface of metals during exposure to air at 200 °C for 4 h. They also subjected a penny (95% Cu, 5% Zn, minted 1962–1982), one half of which was CVD graphene-coated, to a highly oxidising solution of 30% H₂O₂, and found that the surface of the graphene-coated half of the penny suffered no visible change in appearance, whereas the uncoated half got badly tarnished due to oxidation by H₂O₂, confirming graphene to be an effective corrosion-resistant coating. However, different studies on graphene as a corrosion-resistant coating [10,12–15] suggest a great variability in the extent of corrosion resistance of copper due to graphene coating. Singh Raman et al. [10] reported that the graphene coating improved the corrosion resistance of copper by nearly two orders of magnitude, Prasai et al. [12] found the improvement to be only an order of magnitude, and Kirkland et al. [13] reported the improvement to be insignificant. In fact, Schriver et al. [14] and Zhou et al. [15] have categorically reported the corrosion resistance of the graphene-coated copper to be considerably inferior to that of bare copper during long-term exposure to ambient air. Such remarkable variabilities in the corrosion resistance of CVD graphene-coated copper have been attributed to the defects and discontinuities in coating that are commonly present in CVD graphene, such as poor surface coverage, cracks, graphene domain boundaries, and wrinkles [16].

Zhou et al. [15] demonstrated the corrosion resistance of graphene-coated copper to be worse than that of bare copper during a six-month exposure to air. However, Kalita et al. [17] showed that graphene coating provided oxidation resistance to copper when exposed for short durations (1 h) at 150 °C in air. Schriver et al. [14] investigated the durability of oxidation resistance of copper due to graphene coating at 185 and 250 °C. They found graphene to provide corrosion resistance during initial/short exposure but the graphene-coated copper showed inferior corrosion resistance during prolonged exposure. However, a close scrutiny of the results reported in their paper suggests that extensive oxidation during prolonged exposure was limited to locations where graphene was defective/disrupted, whereas the areas where graphene was reasonably defect-free did not suffer oxidation.

The great variability in the extent of corrosion resistance of copper due to graphene coating in the reported studies [1–5] indicates the need for a full surface coverage of graphene for durable corrosion resistance. Wlasny et al. [16] suggested that cracks in the graphene provide windows for nanoscale corrosion and showed such instances of localised corrosion. Hsieh et al. [18], who also reported that nanometre-sized defects in CVD graphene deteriorate corrosion protection, also undertook masking of these defects by atomic layer deposition (ALD) of aluminium oxide on graphene-coated copper, thereby considerably enhancing the corrosion resistance.

Cu-Ni alloys find application in various industries, e.g., coin minting, armaments, desalination, and marine engineering. They are also extensively used in the chemical, petrochemical, and electrical industries due to the specific properties of copper and nickel [19]. They also find uses in piping, heat exchangers and condensers for seawater systems, marine hardware, propellers, and crankshafts and hulls of premium tugboats because of their high corrosion resistance in seawater. When Cu-Ni alloys are used for ships operating in polluted seawater, they often corrode much faster than expected—800 mpy (mils per year)—due to sulphide contamination [20–23].

There are a few studies of the aqueous corrosion of graphene-coated Cu and Ni [10,12,13]. However, there has been no study on the corrosion behaviour of multilayer graphene-coated Cu/Ni alloys in aqueous environment, which may be critical since multilayer graphene can provide better surface coverage, which can potentially improve corrosion resistance.

On the basis of the preceding description of the findings on graphene as a corrosion barrier, we hypothesized that a more effective surface coverage and corrosion resistance may be attained with multilayer graphene. Hence, an increase in the number of graphene layers may play a role in improving corrosion resistance due to a decrease in wettability.

In this study, we experimentally demonstrate that a multilayer graphene coating provides durable corrosion resistance to a Cu-Ni alloy. This is a systematic electrochemical investigation on the aqueous corrosion resistance of the Cu-Ni alloy in a 0.1 M NaCl solution.

2. Methods

2.1. Test Materials

The chemical composition of the Cu-Ni (75/25) alloy used in this study, as shown in Table 1, was determined by Spectrometer Services Pty Ltd. (Coburg, Australia).

Table 1. Chemical composition of the Cu-Ni (75/25) alloy.

Element	Cu	Si	Fe	Zn	Pb	Cr	Ni
wt %	Bal.	0.01	<0.01	0.03	<0.01	<0.01	24.3
Element	Mn	Sn	Al	P	As	Sb	
wt %	0.31	<0.01	<0.01	<0.01	<0.01	<0.01	

The electrolyte used in the electrochemical tests was 0.1 M NaCl solution.

2.2. Chemical Vapour Deposition (CVD) of Graphene on a Cu-Ni Alloy

Discs of the Cu-Ni alloy (thickness ~0.8 mm and diameter 12.5 mm) were polished with SiC paper up to 2500 grit and cleaned with acetone and deionised water. The cleaned discs were placed in the middle zone of the quartz tube of a furnace for CVD of graphene. The quartz tube was first pumped down to a pressure of 70 mTorr, and then a gas mixture of 85% Ar and 15% H₂ was introduced at a pressure of 8–9 Torr and a flow rate of 400 sccm. The reducing atmosphere of H₂ is employed for avoiding oxidation of the Cu-Ni alloy at high temperatures as well as for the reduction of the native oxide layer on the Cu-Ni alloy, thereby providing a pristine alloy surface for graphene deposition. The furnace was heated to 1000 °C at a heating rate of 30 °C/min, while maintaining the reducing atmosphere of Ar/H₂ flow. The Cu-Ni coupons were annealed for 4 min at 1000 °C under a reducing atmosphere, and then the Ar/H₂ flow was replaced with a n-hexane vapour that was passed at 4.4 sccm and 1 Torr for 6 min. Then, the Cu-Ni coupons were cooled under the flow of Ar/H₂ flow at 400 sccm and at a pressure of 8–9 Torr.

The growth conditions of graphene films on a Cu-Ni alloy have been listed in Table 2.

Table 2. Growth conditions for CVD growth of graphene on a Cu-Ni alloy.

Base Pressure/Initial Vacuum	Ar/H ₂ Pressure in Quartz Tube during Heating and Annealing	Flow Rate of Ar/H ₂ both during Annealing and Cooling	Annealing Time
70 mTorr	8–9 Torr	400 sccm	4 min
Reaction Temperature and Heating Rate	Duration of N-Hexane Flow	N-hexane Flow Rate and Pressure	Ar/H ₂ Pressure in Quartz Tube during Cooling
1000 °C and 30 °C/min	6 min	4.4 sccm and 1 Torr	8–9 Torr

2.3. Characterisation of Graphene

The coated samples, developed as described in the preceding section, were characterised using Raman spectroscopy and optical microscopy to search for the presence of graphene and describe the physical properties (morphology and defects).

2.3.1. Raman Spectroscopy

The Cu-Ni samples subjected to CVD treatment were characterised using a Renishaw micro-Raman Spectrometer (Model inVia Renishaw plc, Wotton-under-Edge, UK) that uses a HeNe (632.8 nm) laser operating at 100% power. The Raman spectrometer was also equipped with a microscope and the laser light was coupled with an objective lens of 50×, which was used for exciting the sample as well as collecting the Raman signals. Extended scans (10 s) were performed at a spectral range between the

Raman shifts of $150\text{--}3200\text{ cm}^{-1}$ with a laser spot size of $1\text{ }\mu\text{m}$. Prior to each Raman run, the system was wavenumber-calibrated with the known Raman peak of a solid silicon standard centred at 520.5 cm^{-1} (see Supplementary Materials Figure S1). Subtraction of the baseline using cubic spline interpolation was done in order to eliminate unwanted background noise and facilitate data analysis.

2.3.2. Optical Microscopy

The optical micrographs of bare and graphene-coated Cu-Ni alloys were obtained using an Olympus BX 51 optical microscope (Model BX51TRF, Olympus Corporation, Tokyo, Japan). Optical microscopy enabled observation of the surface coverage of graphene coating on the alloy sample.

2.4. Electrochemical Characterisation

Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were employed for qualitative and quantitative characterisation of corrosion kinetics of graphene-coated and uncoated samples in 0.1 M NaCl , using a Princeton Applied Research (PAR) potentiostat (Model 2273, Princeton Applied Research, Advanced Measurement Technology, Inc., Oak Ridge, TN, USA). All the electrochemical experiments were performed in a conventional three-electrode electrochemical cell (specimens with an exposed area of 0.785 cm^2 acted as the working electrode, platinum mesh as a counter electrode, and saturated calomel electrode as the reference electrode). E_{corr} vs. time plots were generated after immersion in 0.1 M NaCl for 1 h , to ascertain the stabilized open circuit potential (OCP).

2.4.1. Potentiodynamic Polarisation

The cathodic and anodic plots were generated by sweeping the potential on either side of the OCP at a scan rate of 0.1667 mV/s (ASTM F2129-04 [24]) for graphene-coated and uncoated metal samples. The sweeping was carried out over the potential range of $-300/+300\text{ mV}$ for graphene-coated and uncoated Cu-Ni alloy samples.

2.4.2. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) was performed on the graphene-coated and bare samples in a 0.1 M NaCl solution using PAR potentiostat and an electrochemical cell with three electrodes (the cell was described earlier). First, the E_{corr} vs. time plots were generated after immersion in 0.1 M NaCl for 1 h , to ascertain the stabilized open circuit potential (OCP). When the fluctuation of OCP was limited to $<10\text{ mV}$ for a period of 1000 s , the condition was considered stable for the purpose of EIS experiments. EIS runs were carried out by applying a sinusoidal signal at E_{corr} with a perturbation potential of 10 mV . Impedance response was measured over frequencies from 1 MHz to 10 mHz , recording 10 points per decade of frequency using Powersuit software (version 2.58). These frequencies are chosen such that they reach the asymptotic limits, at which the imaginary impedance tends to zero at the lowest and highest frequencies of the employed frequency range.

Impedance analysis was carried out using PAR ZSimpWin (version 3.21) package for Windows for frequencies from $10,000\text{ Hz}$ to 0.1 Hz , which prevented misinterpretation of any artefacts that may be present in the high-frequency region or the scatter in the low-frequency region.

A time-dependent EIS study was carried out after immersion of graphene-coated Cu-Ni alloy in 0.1 M NaCl for different durations ($1, 24, 48, 216, 336\text{ h}$).

3. Results and Discussions

3.1. Characterisation of Graphene

Raman spectroscopy provides confirmatory information on whether the deposited layer is graphene. Ferrari et al. [25] determined for the first time, in 2006, the Raman signature for graphene. Graphene has two characteristic peaks, namely a G peak at 1580 cm^{-1} and a 2D peak at 2700 cm^{-1} . Furthermore, Ni et al. [26] showed that the ratio of intensities of these peaks can determine the number

of graphene layers. The number of graphene layers increases with the ratio of intensities I_G/I_{2D} , and is roughly 0.36 for a single layer and >1 for bi- or multi-layer graphene [27].

The two signature Raman peaks of graphene are a G peak at 1580 cm^{-1} and a 2D peak at 2700 cm^{-1} (Ferrari et al. [25]). The ratio of intensities of the G and 2D peaks (I_G/I_{2D}), i.e., a measure of the number of graphene layers, is ~ 0.5 for a single layer in the case of the Cu-Ni alloy and increases linearly with the number of layers. The I_G/I_{2D} ratio in a typical Raman spectrum in Figure 1 of the graphene films deposited in the present study is 3, which indicates 5–6 layers of graphene (the Raman spectrum in Figure 1 is representative of 5–6 such spectra (see Supplementary Materials Figure S2 for reproducibility)). The thickness of graphene coating in this study is around 1.675–2.01 nm (considering that there were 5–6 layers and the thickness of a single layer of graphene is 0.335 nm). The D-peak at 1350 cm^{-1} signifies the extent of defects in graphene [28]. The relatively high intensity of the D peak in Figure 1 indicates that the graphene layers had considerable defects (such as vacancies and strained hexagonal/non-hexagonal (pentagon or heptagon) distortions that are reported to result in corrugation and twisting of layers [28]).

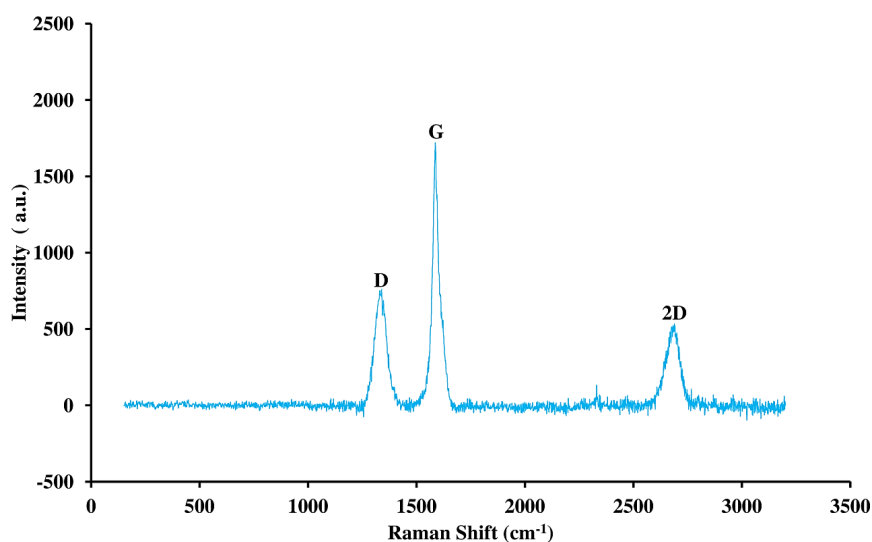


Figure 1. Raman spectrum of a graphene-coated Cu-Ni alloy.

The optical micrographs of bare and graphene-coated Cu-Ni alloy are shown in Figure 2.

Since the annealing time during the CVD process was only 4 min, the extent of thermal etching of grain boundaries of Cu-Ni alloy was limited and the thermally etched grain boundaries of the Cu-Ni alloy are rarely seen (Figure 2b).

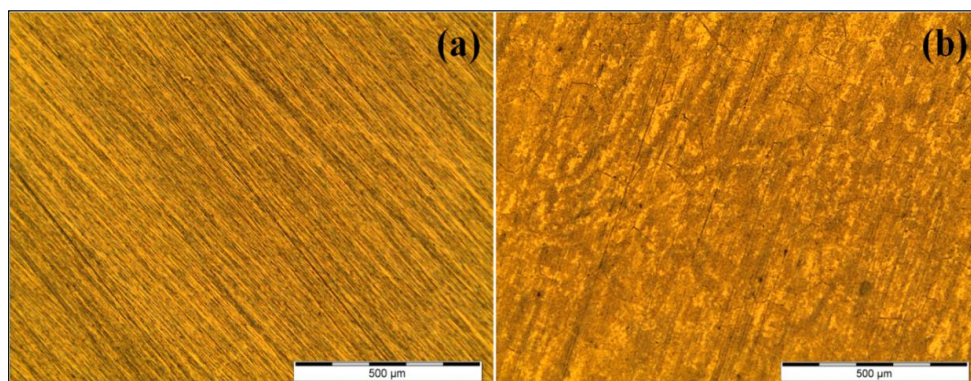
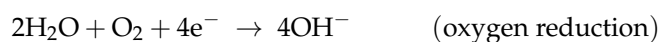


Figure 2. Optical micrographs of (a) bare and (b) graphene-coated Cu-Ni alloy.

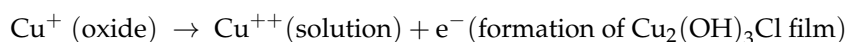
3.2. Electrochemical Characterisation

It is well established that Cu-Ni alloys with sufficient Cu form a corrosion film composed of a thick, porous outer layer of $\text{Cu}_2(\text{OH})_3\text{Cl}$ and a thin, adherent layer of Cu_2O when exposed to aerated chloride solutions [21,22]. The outer layer offers little corrosion protection, while the inner layer provides corrosion protection [21]. During corrosion, the cathodic process of oxygen reduction occurs at the interface between the inner and outer corrosion film [21], as shown below. The anodic reaction of metal oxidation occurs at the interface between the oxide film and base metal [21]. While the above process of oxide formation is proceeding, a separate electrochemical process may be occurring simultaneously at the interface of the outer and inner corrosion product. This process is the dissolution of the oxide [21]. The cathodic process for the oxide dissolution is oxygen reduction, and the anodic process is oxidation of Cu^+ ions in the Cu_2O film to Cu^{++} ions in solution [21]. These Cu^{++} ions, in turn, are responsible for the formation of the porous outer layer of $\text{Cu}_2(\text{OH})_3\text{Cl}$ [21]. Therefore, the corrosion behaviour of Cu-Ni alloys in aerated chloride solutions (e.g., seawater) is governed by the combined electrochemical process of metal oxidation and Cu_2O dissolution [21]. The cathodic and anodic reactions for Cu-Ni alloy are below:

Cathodic reaction:



Anodic reaction:



The potentiodynamic polarization of multilayer graphene-coated Cu-Ni alloy and bare Cu-Ni alloy after 1 h of immersion in 0.1 M NaCl suggested the anodic and cathodic current densities of multilayer graphene-coated Cu-Ni alloy, respectively, to be nearly an order of magnitude lower than the uncoated Cu-Ni alloy (Figure 3), indicating considerable improvement in the corrosion resistance of Cu-Ni alloy due to the graphene coating. The corrosion potential (E_{corr}) of the multilayer graphene-coated Cu-Ni alloy was 60 mV higher than that of the bare Cu-Ni alloy (Figure 3). E_{corr} is the measure of corrosion susceptibility, and, thus, a positive shift in E_{corr} strongly indicates the corrosion protection ability of the graphene coating. The presence of noise in the cathodic region (absent in the anodic region) of the graphene-coated Cu-Ni alloy is instrumental noise, unlike electrochemical noise. The electrochemical noise persists up to the pitting potential [29]. The instrumental noise was not observed in the case of the uncoated Cu-Ni alloy because these measurements were in the coarser range of the current measurement. The vertical part of the uncoated Cu-Ni alloy at a very negative potential is the diffusion-controlled cathodic reaction, which is a very common phenomenon for all tests (one would make a similar observation for graphene-coated Cu-Ni alloy if one were to undertake a run from negative potential similar to that of the Cu-Ni alloy).

Electrochemical impedance spectroscopy (EIS) provides a quantitative measurement of impedance (polarisation resistance) of bare and coated metals and alloys in response to a very small perturbation of the potential in an AC system. Because the perturbation potentials are very small (typically, 10 mV), EIS is a non-destructive technique for the detailed evaluation of the time-dependent electrochemical phenomena at interfaces, such as those that concern corrosion and coatings, viz., metal/electrolyte, coating/electrolyte, metal/coating interfaces. Quantitative determination of characteristic parameters such as capacitance, resistance, etc., involves a simulation of the experimental EIS data, employing an appropriate equivalent electrical circuit (EEC) based on hypothetical corrosion mechanism. The relative magnitudes of these interfacial resistances and capacitances provide insight into the corrosion protection provided by a film/coating and associated mechanism. The three main criteria to be fulfilled while choosing an appropriate EEC for corrosion process are: (i) a low chi-square value

(typically of the order of 10^{-3} or lower); (ii) minimum total error and relative error in the calculation of individual parameters; and (iii) consistency with a corrosion mechanism [30]. The experimental EIS data are simulated for the chosen EEC using complex nonlinear least square (CNLS) fitting method, as described in [30].

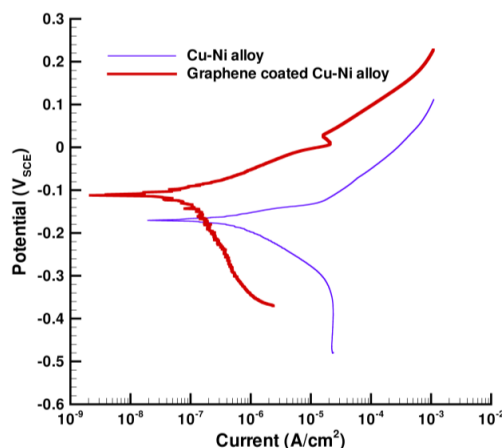


Figure 3. Potentiodynamic polarisation curve for graphene-coated and uncoated Cu-Ni alloy in 0.1 M NaCl.

The diameter of the semicircle of a Nyquist plot and the magnitude of impedance at the lowest frequency in a Bode impedance plot are broad measures of the corrosion resistance. The Bode and Nyquist plots of graphene-coated and uncoated Cu-Ni alloy (Figures 4 and 5) demonstrate the corrosion resistance of the graphene-coated Cu-Ni alloy to be an order of magnitude greater than that of the bare Cu-Ni alloy. It has been argued that multilayer graphene can provide durable corrosion resistance [31]. Accordingly, the considerable improvement in corrosion resistance of graphene-coated Cu-Ni alloy (Figures 4 and 5) is attributed to the multilayer graphene (as established by the Raman spectrum in Figure 1). The Bode phase plots for graphene-coated and uncoated Cu-Ni alloys during a 1 h immersion in 0.1 M NaCl solution are presented in Figure 6. The broad phase angle peaks in the Bode phase plots suggest a merger of two time constants in each case. The two time constants are attributed to the coating/solution interface and the metal/solution interface in the case of the graphene-coated Cu-Ni alloy, whereas they are ascribed to corrosion products/solution interface and metal/solution interface in the case of the bare Cu-Ni alloy [10].

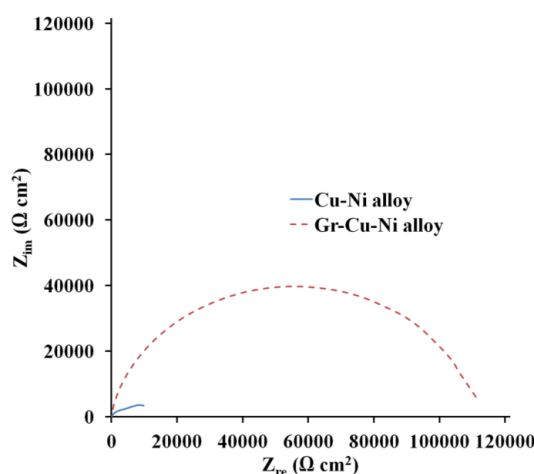


Figure 4. Nyquist plots showing the corrosion resistance of bare and graphene-coated Cu-Ni alloy in 0.1 M NaCl.

It is important to note that graphene in the study of Singh Raman et al. [10] was mono- to bi-layer, as compared to the few layers of graphene in this study (as confirmed by the Raman spectrum in Figure 1). A comparison of the polarization and EIS data in Figures 3–5 and those in the study of Singh Raman et al. [10] would suggest the corrosion resistance achieved in the two studies was comparable, in spite of the considerable defects in the coating in this study (Figure 1). The considerable corrosion resistance due to graphene coating in this study is attributed to the multilayer graphene.

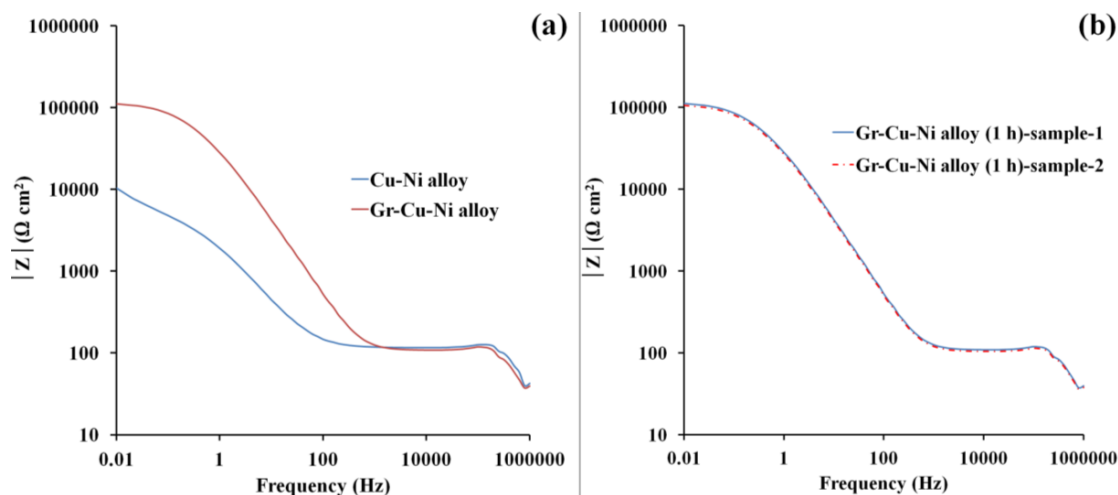


Figure 5. Bode plots: (a) for bare and graphene-coated Cu-Ni alloy (Gr-Cu-Ni); and (b) duplicate plots for graphene-coated Cu-Ni alloy showing reproducibility, in 0.1 M NaCl.

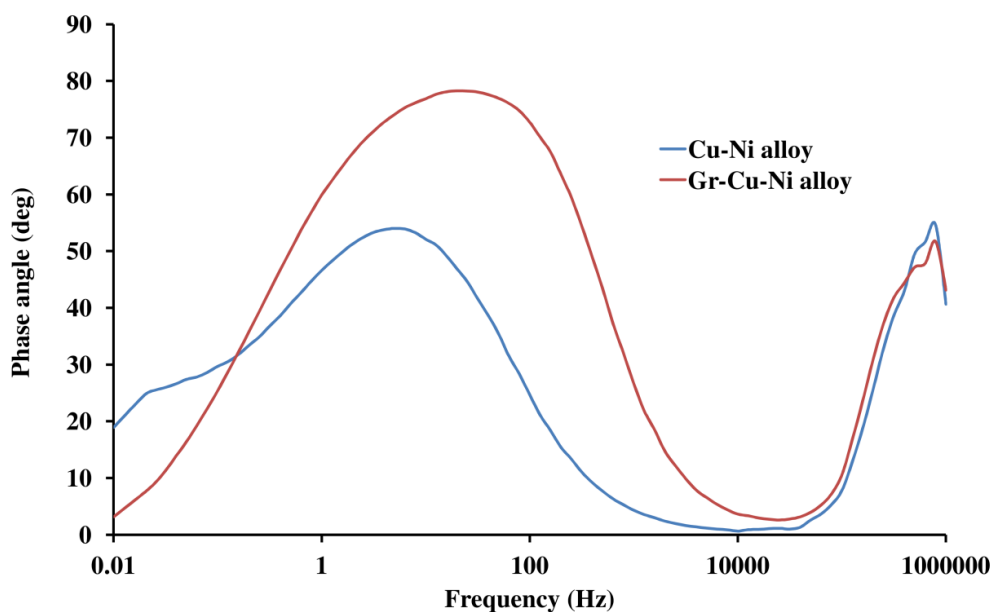


Figure 6. Bode phase angle plots for bare and graphene-coated Cu-Ni alloy (Gr-Cu-Ni) in 0.1 M NaCl.

3.3. Durable Corrosion Resistance due to Graphene Coating

It is still of great technical importance to investigate whether the corrosion resistance due to graphene coating after 1 h of immersion in 0.1 M NaCl solution could be sustained for longer durations. Thus, an EIS study was carried out in 0.1 M NaCl after an extended period of immersion (24, 48, 216, 336 h) in 0.1 M NaCl. The Bode impedance plots in Figure 7 demonstrate the improvement in corrosion resistance (i.e., impedance at the lowest frequency) due to graphene coating by an order of magnitude

after 1 h of immersion in 0.1 M NaCl to be maintained even after a long immersion period of 336 h. As shown in Figure 7b–e, the impedance spectra are quite reproducible.

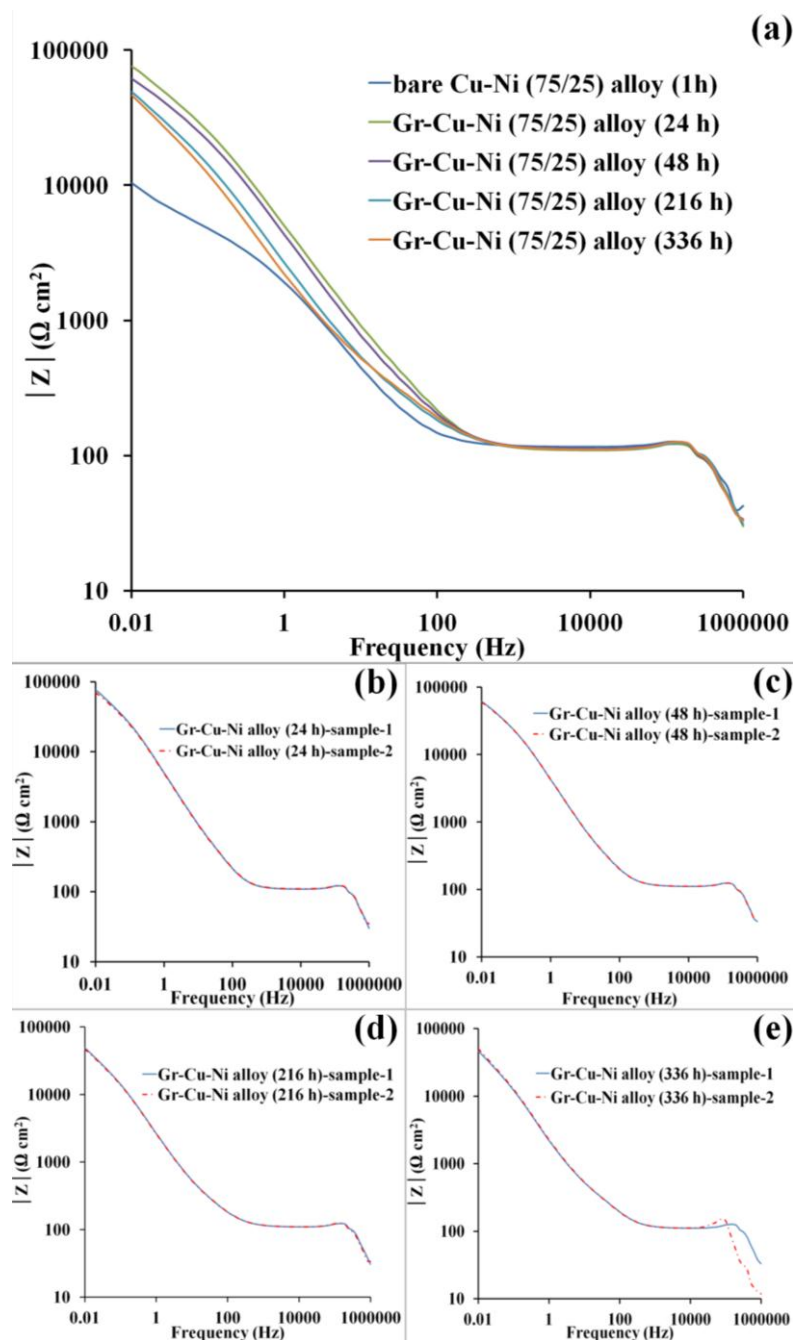


Figure 7. (a) Bode modulus plots for bare Cu-Ni alloy and graphene-coated Cu-Ni alloy (Gr-Cu-Ni) in 0.1 M NaCl (Note: the bare Cu-Ni alloy was only immersed for 1 h); and (b–e) Bode modulus plots showing the reproducibility of data after immersion for (b) 24 h, (c) 48 h, (d) 216 h, and (e) 336 h.

The broad phase angle peaks in Bode phase plots after different durations of immersion are attributed to two time constants in each case (Figure 8). As described earlier, the two time constants are ascribed to the presence of the two interfaces, i.e., the graphene coating/solution interface and the metal/solution interface in the case of the graphene-coated Cu-Ni alloy, while the two time constants are due to the development of metal hydroxide/oxide films, i.e., corrosion products/solution

interface and metal/solution interface in the case of the bare Cu-Ni alloy. The Bode phase plots after different immersion times have a similar magnitude of phase maximum; however, the phase maximum gradually shifts towards a lower frequency with increasing immersion periods, which is attributed to the increase in the amount of corrosion products over time. The constant nature of the Nyquist and Bode plots for the graphene-coated Cu-Ni alloy through the entire period of immersion, 1–336 h (Figures 7 and 8), and the reproducibility of the data confirmed the ability of a multilayer graphene coating to provide corrosion resistance in the long term.

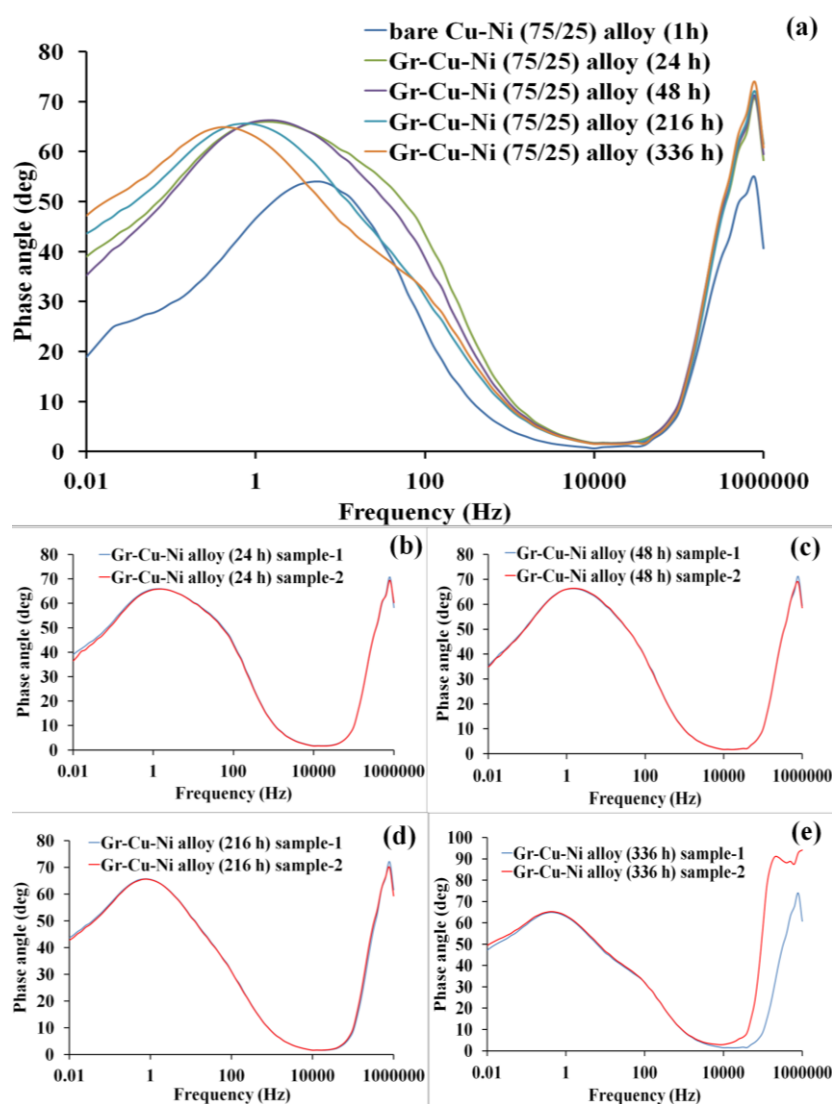


Figure 8. (a) Bode phase plots for bare and graphene-coated Cu-Ni alloy (Gr-Cu-Ni) in 0.1 M NaCl (Note: the bare Cu-Ni alloy was only immersed for 1 h); and (b–e) Bode modulus plots showing the reproducibility of data after immersion for (b) 24 h; (c) 48 h; (d) 216 h; and (e) 336 h.

Simulation of experimental EIS data was carried out to quantitatively determine the characteristic parameters like capacitance, charge transfer resistance, pore resistance, etc. using a proper equivalent electrical circuit (EEC), taking into account a speculative corrosion mechanism. An EEC with two time constants is shown in Figure 9. There are two time constants: one in the high-frequency region corresponds to the graphene coating/solution and another in a lower-frequency region corresponds to the metal/solution interface.

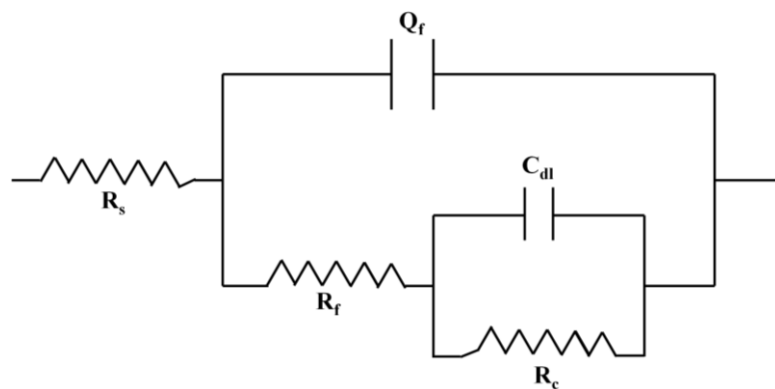


Figure 9. Equivalent electrical circuit (EEC) for corrosion of bare and graphene-coated Cu-Ni alloy.

The EEC shown in Figure 9 was picked as a result of the interconnected nature of the coating defects (for example: graphene grain boundaries for graphene-coated Cu-Ni alloy or oxide/hydroxide porosity for bare Cu-Ni alloy). In the EEC, R_s is the solution resistance, Q_f and R_f represent the constant phase element (CPE) and the film resistance in parallel combination to represent graphene coating, respectively, C_{dl} is the electrical double layer capacitance, and R_c is the charge transfer resistance. The CPE conduct is by and large credited to the distributed surface reactivity, roughness, and electrode porosity [30,32]. The PAR ZSimp package for Windows was used for impedance investigation between frequencies 10,000 Hz and 0.1 Hz. The characteristic EEC parameters are presented in Table 3.

Table 3. Quantitative analysis of EIS data using model EEC: $R_s(Q_f[R_f(C_{dl}R_c)])$ as in Figure 9.

Sample, Immersion Time	R_f (Ω cm ²)	R_c (Ω cm ²)	Q_f (F/cm ²)	n	C_{dl} (F/cm ²)	Chi Squared Value	Total Error (%)	Corrosion Resistance ($R_f + R_c$) (Ω cm ²)
Bare Cu-Ni, 1 h	4.806×10^3	3.620×10^3	1.002×10^{-4}	0.7796	7.202×10^{-4}	8.626×10^{-4}	2.937	8.426×10^3
Gr-Cu-Ni, 1 h	5.957×10^4	4.274×10^4	4.972×10^{-6}	0.93	1.453×10^{-5}	1.362×10^{-3}	3.69	10.231×10^4
Gr-Cu-Ni, 24 h	1.145×10^4	6.277×10^4	4.387×10^{-5}	0.7743	3.308×10^{-6}	5.929×10^{-4}	2.435	7.422×10^4
Gr-Cu-Ni, 48 h	4.749×10^3	5.677×10^4	5.128×10^{-5}	0.7712	3.407×10^{-6}	2.102×10^{-4}	1.45	6.152×10^4
Gr-Cu-Ni, 216 h	1.720×10^3	6.57×10^4	8.097×10^{-5}	0.7364	1.036×10^{-5}	1.461×10^{-4}	1.209	6.742×10^4
Gr-Cu-Ni, 336 h	1.742×10^3	1.01×10^5	9.388×10^{-5}	0.7009	1.908×10^{-5}	5.357×10^{-4}	2.314	10.274×10^4

Table 3 reveals that the corrosion resistance of multilayer graphene-coated Cu-Ni alloy, an aggregate of pore resistance and the resistance offered by the interface of multilayer graphene and electrolyte (R_c), is $10.231 \times 10^4 \Omega$ cm², $7.422 \times 10^4 \Omega$ cm², $6.152 \times 10^4 \Omega$ cm², $6.742 \times 10^4 \Omega$ cm², and $10.274 \times 10^4 \Omega$ cm² for the immersion periods of 1, 24, 48, 216, and 336 h, respectively and that of the uncoated/bare Cu-Ni alloy is $8.426 \times 10^3 \Omega$ cm² (for the bare Cu-Ni alloy, it is the sum of pore resistance and the resistance offered by the metal/electrolyte interface).

The data in Table 3 confirm that multilayer graphene coating improves corrosion resistance of a Cu-Ni alloy by an order of magnitude and this improvement in corrosion resistance is sustained for long periods of immersion (336 h), which is consistent with the Bode plots in Figure 5. The lower Q_f of multilayer graphene indicates a lower number of conductive pathways in multilayer graphene coating and the relatively lower C_{dl} of multilayer graphene coating demonstrates the lower exposure of the metal/electrolyte interface. The exponent of CPE is close to 1, showing the almost completely capacitive nature of graphene coating. The low chi-squared value indicates the reasonable accuracy of EEC parameters obtained by EIS data simulation. Figure 10a–c demonstrates the fitting of simulated EIS data with the experimental EIS data of a graphene-coated Cu-Ni alloy for immersion periods of 1 h, 48 h, and 336 h, respectively. The experimental data match well with the simulated data in the frequency range from 10,000 Hz to 0.1 Hz, as is evident from Figure 10. The total error in the impedance analysis in the simulation of experimental data when utilizing EEC (Figure 9) was under 4%

in all simulations. The low associated chi-squared values and low total error confirm the legitimacy of the utilised EEC (Figure 9) and corrosion mechanism for graphene-coated and uncoated Cu-Ni alloys.

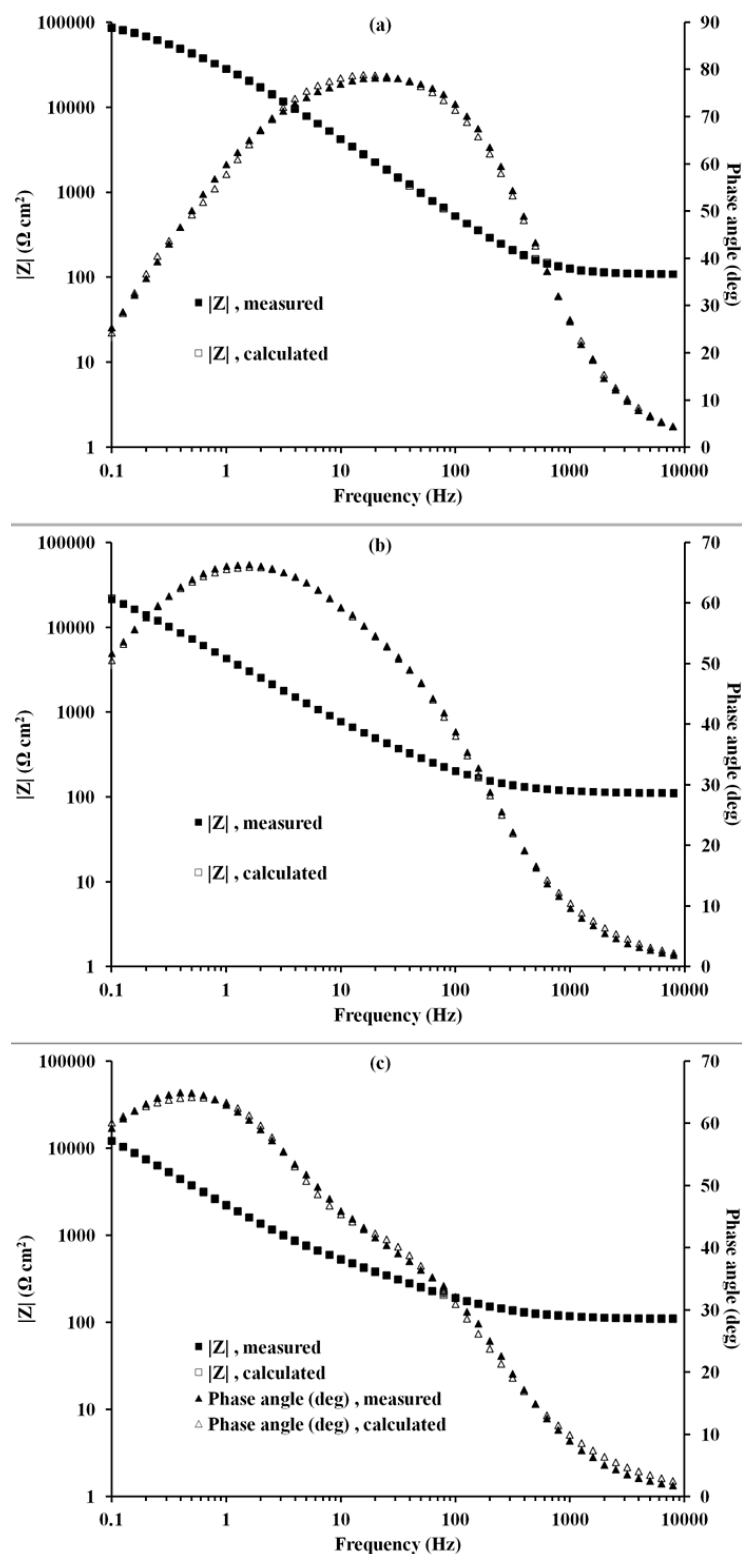


Figure 10. Curve fitting of experimental and simulated Bode plots for graphene-coated Cu-Ni alloy after immersion in 0.1 M NaCl for (a) 1 h, (b) 48 h, and (c) 336 h.

4. Conclusions

Graphene coating was successfully synthesized on a Cu-Ni alloy using the chemical vapour deposition technique. Electrochemical tests indicated that the multilayer graphene coating acted as a considerable corrosion barrier for the Cu-Ni alloy and provided a durable corrosion protection in 0.1 M NaCl. The corrosion resistance conferred by the multilayer graphene coating on Cu-Ni alloy was sustained for an extended duration (up to 336 h). In this context, it is important to note that the graphene coating has been reported to provide insignificant improvement in corrosion in a few studies. In fact, some reports have suggested a deterioration in corrosion resistance due to graphene coating. Such contradictory findings, as reported in the literature, could be addressed thoroughly through the findings of this study. The inferior or insignificant corrosion resistance due to graphene coating is attributed to the poor quality of graphene (to be precise, the extent of surface coverage and the defect content of the graphene coating). The suggestion in the present study that multilayer graphene (instead of single layer graphene) can provide a superior surface coverage and durable corrosion resistance to the Cu-Ni alloy was found to be valid. The reason for superior corrosion resistance with multilayer graphene is that the pores/defects in single-layer graphene that were responsible for the deterioration in corrosion resistance could be blocked by the subsequent over-layer, thereby improving the corrosion resistance.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2079-6412/7/12/210/s1>. Figure S1. (a) Raman spectrum of solid silicon standard showing Raman peak at 520.5 cm^{-1} , which indicates that the Raman system is wavenumber-calibrated; (b) optical micrograph of solid silicon; and (c) optical micrograph of laser spot; Figure S2. Raman spectrum of a graphene-coated Cu-Ni alloy at different spots showing the uniformity of graphene over the sample surface.

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Author Contributions: Abhishek Tiwari conceived the idea and designed and built the CVD reactor for graphene synthesis, planned and performed the experiments, analysed the experimental data, and wrote the manuscript. R. K. Singh Raman directed and supervised the research and provided help for editing the manuscript and provided useful insights into the manuscript.

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