



Synergistic corrosion Inhibition of interfacially engineered Al-O/CNT composites through Al-O-C chemical anchoring



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Enhancing the corrosion resistance of aluminum (Al) matrix composites remains a significant challenge due to the inherent interfacial instability between the matrix and carbon nanotubes (CNTs). This study reports a superior corrosion inhibition mechanism in interfacially engineered Al-O/CNT composites, driven by the formation of robust Al-O-C chemical anchoring. We comparative analyzed the electrochemical degradation of pure Al, Al/CNT, and Al-O/CNT through salt spray tests and density functional theory (DFT) simulations. SEM analysis revealed that the Al-O/CNT composite exhibited the thinnest corrosion layer 0.45 μm , significantly outperforming Al/CNT (0.86 μm) and pure Al (2.45 μm). Furthermore, the Al-O/CNT composite demonstrated a negligible net mass gain of only 0.15 mg/cm^2 , which is significantly lower than those of Al/CNT (1.84 mg/cm^2) and pure Al (2.12 mg/cm^2). XPS analysis demonstrated that the Al-O-C interface effectively suppresses the hydration of the Al_2O_3 passive film into unstable $\text{Al}(\text{OH})_3$, while enabling a near-complete (99.8%) immobilization of metal chlorides at the interface to prevent deep Cl^- penetration. DFT calculations corroborated these findings, revealing a thermodynamic shift from weak mechanical interlocking (-3.52 eV) to stable chemical anchoring (-5.72 eV). This high interfacial binding energy provides an electronic barrier against electrolyte ingress and stabilizes the protective oxide layer. The synergistic effect of the physical CNT network and the chemically anchored interface establishes a multi-level defense system, offering a new paradigm for designing highly corrosion-resistant metal matrix composites.

Aluminum matrix composites (AMCs) reinforced with carbon nanotubes (CNTs) have emerged as a cornerstone of next-generation materials science, offering an unparalleled combination of low density, high specific strength, and exceptional thermal conductivity. These properties have positioned CNT-reinforced AMCs as ideal candidates for critical structural components in the aerospace, automotive, and high-performance electronics industries^{1,2}. Despite their extraordinary mechanical potential, the widespread industrial adoption of these composites is severely restricted by a fundamental durability flaw: their heightened susceptibility to localized

corrosion in aggressive chloride-containing environments. The corrosion resistance of aluminum and its alloys primarily relies on the formation of a thin, dense, and protective native oxide (Al_2O_3) passive film. However, in the context of metal matrix composites (MMCs), the introduction of CNTs significantly complicates this protective mechanism^{3,4}.

The electrochemical disparity between the chemically noble CNTs and the highly active aluminum matrix creates a multitude of micro-galvanic cells at the interface⁵. In these cells, the aluminum matrix acts as the anode, while the conductive CNTs serve as the cathode, leading to localized

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dissolution and the acceleration of pitting corrosion^{6–8}. Furthermore, the lack of intrinsic chemical affinity between C and Al often resulting in poor wettability, which fosters a mechanical interlocking state rather than a true chemical bond. This weak interfacial contact leaves nanometer-scale gaps and electronic diffusion paths that corrosive electrolytes, such as Cl[−] ions and H₂O molecules, can easily penetrate.

Historically, the majority of research regarding the interfacial engineering of AMCs has been directed toward mechanical optimization. Strategies such as surface functionalization of CNTs or the controlled formation of Al₄C₃ carbides have been extensively studied to enhance load transfer and tensile strength. However, the influence of interfacial design on electrochemical stability has remained largely unexplored and often treated as a secondary concern. Most conventional AMCs fail prematurely in salt spray environments because their passive films are prone to rapid hydration. Under chloride attack, the protective Al₂O₃ layer is transformed into porous and non-protective aluminum hydroxide (Al(OH)₃), which swells and loses its structural integrity, leading to a total loss of surface passivity^{9–11}.

To address these critical limitations, this study proposes a paradigm-shifting strategy: the transition from mechanical interlocking to Al-O-C chemical anchoring^{12,13}. By strategically engineering an oxide-bridged interface, we have created a multi-level defense system that simultaneously addresses both the physical and electrochemical aspects of corrosion inhibition. The core of this innovation lies in the thermodynamic stabilization of the interface. Through advanced density functional theory (DFT) simulations, we demonstrate that the formation of Al-O-C bonds shifts the interfacial binding energy from a relatively unstable −3.52 eV (characteristic of mechanical interlocking) to a profoundly stable −5.72 eV (chemical anchoring). This energetic descent represents a quantum leap in thermodynamic stability, creating an impenetrable energy well that corrosive agents cannot easily disrupt.

Our experimental results validate this theoretical framework with unprecedented clarity. In rigorous salt spray testing, the interfacially engineered Al-O/CNT composites exhibited a remarkably thin corrosion layer of just 0.45 μm. The superior performance of the Al-O/CNT system is further elucidated through microstructural evaluation including high-resolution X-ray photoelectron spectroscopy (XPS). In summary, this work provides a comprehensive atomic-to-macro scale understanding of how interfacial chemical bonding dictates the corrosion longevity of metal matrix composites. By moving beyond the conventional focus on mechanical properties, we demonstrate that interfacial engineering through chemical anchoring is the key to unlocking the full potential of MMCs in harsh environments.

Results

Macro-scale corrosion resistance

To establish a rigorous baseline for microstructural comparison, the matrix grain size of the Pure Al sample was evaluated in a representative region, yielding a grain diameter of 29.41 μm, as shown in Fig. S2. In contrast, both the conventional Al/CNT and interfacially engineered Al-O/CNT composite samples exhibited significant grain refinement. This refinement is primarily attributed to the Zener pinning effect exerted by the uniformly dispersed CNTs and oxides along the matrix grain boundaries during high-energy ball milling and subsequent hot-pressing consolidation. To quantitatively evaluate the long-term durability and electrochemical stability of the composites, a salt spray test was conducted followed by potentiodynamic polarization analysis. Table 1 summarizes the mass change of the specimens after the 48 h salt spray exposure. The Al-O/CNT composite exhibited the

lowest mass change (0.04%), which is approximately 98% lower than that of pure Al (6.13%) and significantly improved compared to the Al/CNT composite (0.19%). This clear reduction in mass change suggests that the interfacial engineering in Al-O/CNT effectively establishes a superior barrier against the aggressive electrolyte.

The electrochemical kinetics were further investigated using potentiodynamic polarization curves, as shown in Fig. 1. The corresponding electrochemical parameters, including corrosion potential (E_{corr}) and corrosion current density (i_{corr}), are tabulated in the inset of Fig. 1. The E_{corr} values showed a distinctive noble shift as the interface was engineered: from −0.89 V for pure Al to −0.79 V for Al/CNT, reaching the most positive value of −0.75 V for Al-O/CNT. This positive shift in E_{corr} indicates that the Al-O/CNT surface is thermodynamically more stable and less prone to the initiation of electrochemical dissolution compared to the other specimens. While the i_{corr} of Al-O/CNT (8.59 μA/cm²) is slightly higher than that of pure Al, this is attributed to the increased cathodic surface area provided by the conductive CNT network; however, the simultaneous shift to a more noble potential and the significantly reduced mass change confirm that the overall corrosion rate is effectively suppressed by the stabilized passive film. Previous studies have reported that the passive film formed on aluminum surfaces can exhibit semiconducting behavior, where its electrochemical characteristics are intrinsically linked to point defects within the film. Specifically, the passive film formed on pure aluminum in a 3.5 wt.% NaCl solution was confirmed via Mott-Schottky analysis to exhibit n-type semiconducting characteristics, with oxygen vacancies and interstitial cations identified as the predominant point defects. Furthermore, a lower point defect density has been demonstrated to suppress electron transport and diminish localized electrochemical reactivity^{14,15}.

The visual degradation and phase changes after the salt spray test are shown in Fig. 2. Before the test, all specimens exhibited smooth, metallic surfaces (Fig. 2a–c). However, after 48 hours of exposure, the pure Al (Fig. 2d) and Al/CNT (Fig. 2e) specimens were covered with extensive white corrosion products and noticeable pitting. In contrast, the Al-O/CNT composite (Fig. 2f) maintained a relatively clean surface with minimal localized damage. The corresponding XRD patterns (Fig. 2g) further support these observations; the pure Al specimen showed prominent peaks associated with Al(OH)₃, whereas these peaks were markedly suppressed in the Al-O/CNT composite, indicating that the Al-O-C anchoring prevents the hydration of the protective Al₂O₃ layer.

To precisely quantify the surface damage, 3D surface morphology and profile analyses were performed (Fig. 3). The 3D images and corresponding line profiles clearly differentiate the pitting characteristics of each specimen. Pure Al (Fig. 3a) suffered from deep, irregular craters exceeding 20 μm in depth and high surface roughness (R_a), representing severe localized breakdown. Al/CNT (Fig. 3b) showed an improved but still inconsistent profile. Most remarkably, the Al-O/CNT composite (Fig. 3c) exhibited the most uniform surface topography, with a significantly reduced maximum pit depth of less than 5 μm. This quantitative topographic data aligns perfectly with the minimal mass change in Table 1. The quantitative profile graphs reveal that the surface fluctuations in Al-O/CNT are remarkably suppressed, consistent with the minimal mass gain observed in Table 1. This enhancement in macro-scale corrosion resistance is not merely a result of the physical barrier effect of the CNTs, but is fundamentally driven by the Al-O-C chemical anchoring, which prevents the breakdown of the protective oxide layer and stabilizes the interface against chloride penetration.

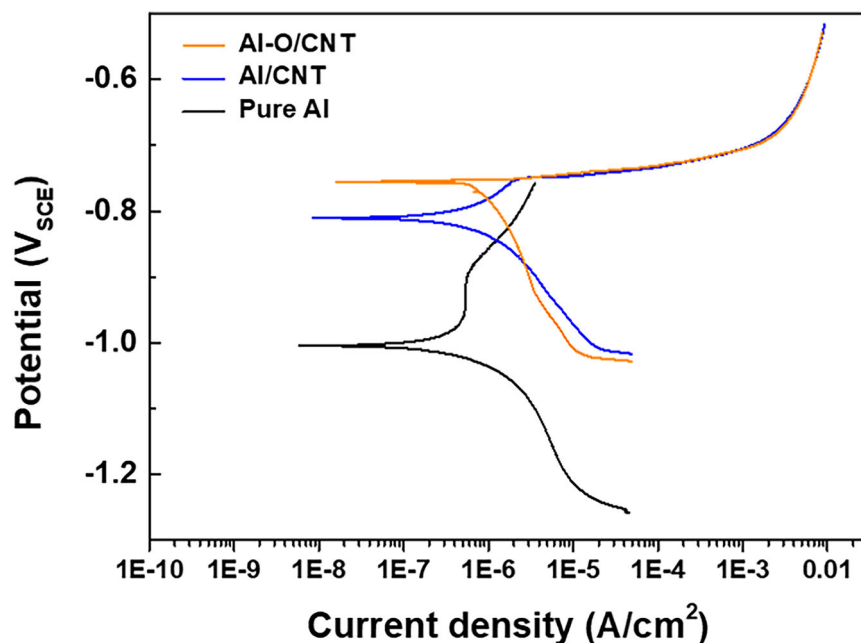
Interfacial microstructures

To elucidate the fundamental mechanisms behind the enhanced corrosion resistance, the cross-sectional morphologies and elemental distributions were analyzed following the 48 h salt spray test. Figure 4 presents the high-magnification SEM cross-sections, providing a quantitative comparison of the corrosion product layer thickness. For the pure Al specimen (Fig. 4a), a thick and highly non-uniform corrosion layer was observed, with thicknesses ranging from 1.54 μm to 2.45 μm. The irregular and porous nature of this layer suggests the unhindered hydration of the passive film into a

Table 1 | Mass change of specimens after salt spray test

Specimen	Before test (g)	After test (g)	Mass change (%)
Pure Al	1.6508	1.7586	6.13
Al/CNT	1.7644	1.7677	0.19
Al-O/CNT	2.003	2.0038	0.04

Fig. 1 | Polarization curves of the specimens.



Specimen	i_{corr}	E_{corr}
Pure Al	6.23	-0.89
Al/CNT	7.31	-0.79
Al-O/CNT	8.59	-0.75

voluminous $\text{Al}(\text{OH})_3$ phase, which fails to provide an effective barrier against electrolyte ingress. In contrast, the introduction of CNTs significantly altered the corrosion kinetics. The standard Al/CNT composite (Fig. 4b) showed a markedly reduced layer thickness, averaging approximately $0.72\ \mu\text{m}$. However, the most profound stabilization was observed in the Al-O/CNT composite (Fig. 4c), which maintained an exceptionally thin and dense corrosion layer with a highly uniform thickness of approximately $0.50\ \mu\text{m}$. This represents a four-fold reduction in thickness compared to pure Al, directly correlating with the minimal mass change and noble E_{corr} shift discussed in Macro-scale corrosion resistance. The elemental distribution within these layers was further investigated using EDS mapping and point analysis, as illustrated in Fig. 5. In the pure Al specimen (Fig. 5a), the EDS mapping reveals a high concentration of Oxygen (O) and Sodium (Na) throughout the thick corrosion layer. Notably, the presence of Chlorine (Cl) at Point #1 (5.1 wt%) indicates deep penetration of Cl^- ions into the porous corrosion products, confirming the lack of an effective chemical barrier. For the Al/CNT composite (Fig. 5b), the Carbon (C) mapping confirms the distribution of CNTs near the interface. While the O-rich layer is thinner than that of pure Al, the interface still shows signs of localized oxidation. In stark contrast, the Al-O/CNT composite (Fig. 5c) exhibits a unique elemental profile. The EDS point analysis at the interface (Points #9 and #10) shows a significant presence of both Carbon (20.6–30.9 wt%) and Oxygen (31.9–40.7 wt%), yet strikingly, Chlorine is virtually absent in these regions. This absence of chloride penetration at the Al-O/CNT interface, despite the aggressive salt spray environment, provides compelling evidence for the Al-O-C chemical anchoring mechanism. While the CNTs in the Al/CNT specimen provide a tortuous physical path for ions, they cannot prevent the atomic-scale diffusion of Cl^- . However, in the Al-O/CNT

system, the pre-existing oxide bridge forms a thermodynamically stable Al-O-C network that acts as a chemical trap. This network stabilizes the metal chlorides at the very top of the interface—as corroborated by the near-complete anchoring observed in the XPS data—effectively sealing the Al matrix from further deleterious hydration and pitting. Consequently, the Al-O/CNT composite maintains a pristine substrate (Point #12, 88.6 wt% Al) even after prolonged exposure, establishing a new standard for interfacial protection in metal matrix composites.

XPS analysis of surface chemical states

To further elucidate the atomic-scale chemical environment and the role of the Al-O-C bridge in corrosion inhibition, high-resolution XPS analysis was performed on the surface of the specimens after the salt spray test. Figure 6 illustrates the deconvoluted spectra of Al 2p, O 1s, and Cl 2p, with the corresponding bonding fractions summarized in Fig. 6d. The Al 2p spectra (Fig. 6a) provide a direct measure of the integrity of the protective passive film. The peaks were deconvoluted into Al-O (oxide) and Al-OH (hydroxide) components^{16,17}. For the Al-O/CNT composite, the Al-O fraction reached a maximum of 58.76%, which is significantly higher than that of Al/CNT (44.80%) and pure Al (55.39%). Conversely, the Al-OH fraction, a marker of passive film degradation, was minimized to 41.24% in the Al-O/CNT system. This suggests that the pre-existing Al-O-C chemical bridge thermodynamically stabilizes the Al_2O_3 lattice, effectively suppressing its hydration into the non-protective $\text{Al}(\text{OH})_3$ phase. The O 1s spectra (Fig. 6b) further corroborate this stabilization mechanism. The fraction of lattice oxygen (O^{2-}), representing the stable oxide framework, was highest in the Al-O/CNT composite (19.21%), nearly double that of pure Al (10.91%)^{18,19}. While the Al/CNT specimen exhibited a high level of adsorbed

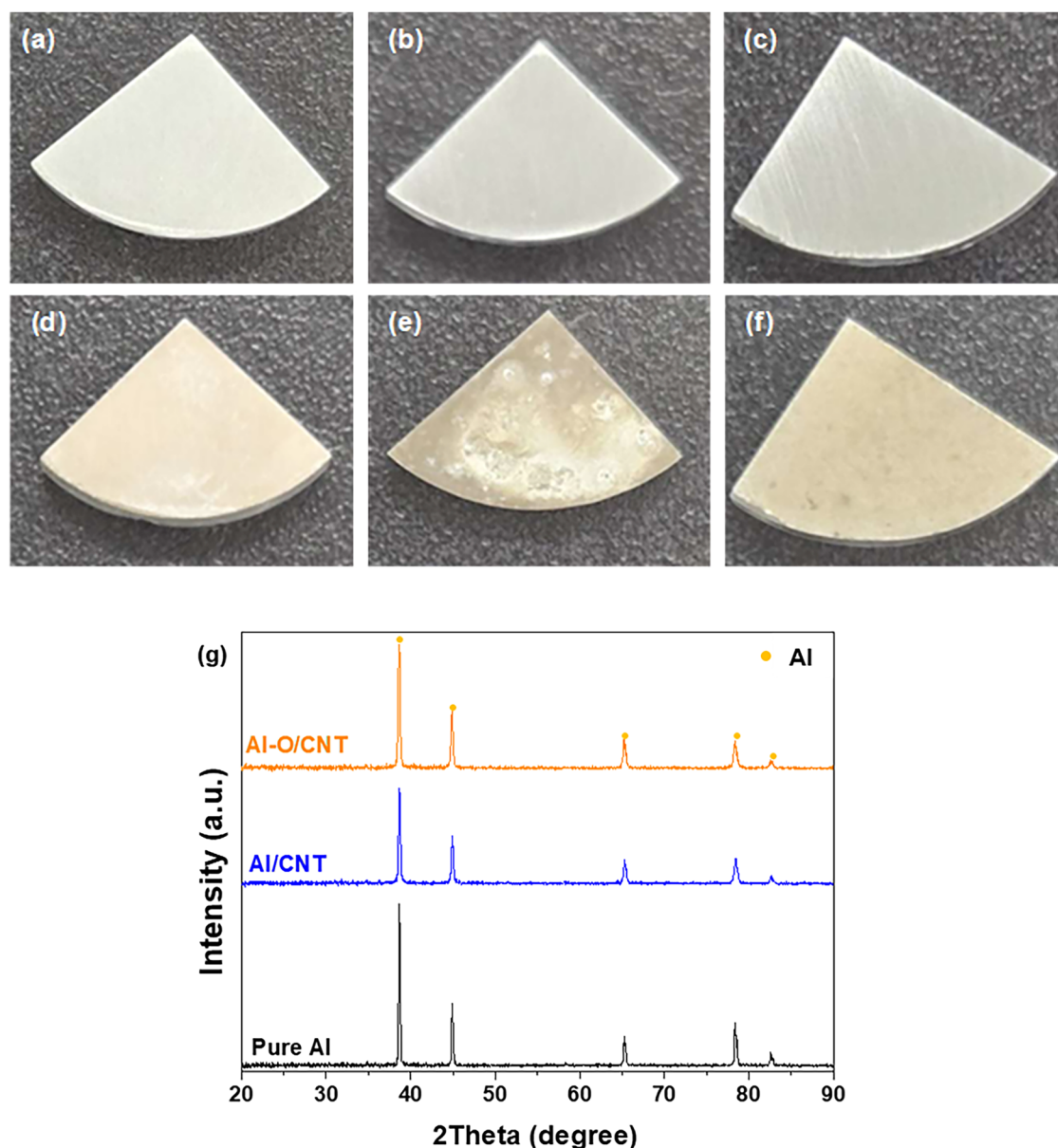


Fig. 2 | Corrosion morphology of specimens (a–c) before and (d–f) after salt spray test. a and d Pure Al, b and e Al/CNT, and c and f Al-O/CNT, and (g) XRD patterns of specimens after salt spray test.

water H_2O and OH^- species, the Al-O/CNT composite maintained a more robust oxide structure. This high O^{2-} content is a direct consequence of the Al-O-C chemical anchoring, which prevents the structural breakdown of the oxide layer even under aggressive chloride attack. The most striking evidence of interfacial protection is found in the Cl 2p spectra (Fig. 6c). While pure Al and Al/CNT show a significant presence of organic or physisorbed chlorides, the Al-O/CNT composite exhibits an overwhelming metal chloride fraction of 99.8%. In conventional corrosion models, a high chloride signal is often associated with severe pitting. However, in this interfacially engineered system, the high metal chloride fraction represents the anchoring of Cl^- ions at the very top of the Al-O-C interface. By capturing the chloride ions into stable metal-halide complexes at the surface, the Al-O-C network prevents their inward diffusion toward the Al matrix.

This chemical trapping mechanism explains why the Al-O/CNT composite retains the thinnest corrosion layer ($0.45\ \mu\text{m}$) despite the high surface chloride concentration. The synergistic integration of the Al-O-C bond energy ($-5.72\ \text{eV}$) and the resulting thermodynamic stability of the O^{2-} lattice establishes an impenetrable chemical barrier, providing a

definitive explanation for the superior macro-scale corrosion resistance observed in this study.

Discussion

DFT calculations were performed to investigate the effect of oxygen incorporation on the interfacial bonding between the Al surface and CNTs. To simulate the adsorption of CNTs on the Al surface, a graphene nanoribbon (GNR) model was employed. In our experimental synthesis, the multi-walled CNTs possess a large average diameter of approximately 20 nm, where the local surface curvature asymptotically approaches the planar limit (0°). Previous computational benchmarking studies have validated that the interfacial binding properties reach an energetic plateau at this planar limit, as the alteration in adsorption energy within the low-curvature regime is minimal^{20,21}. Because such large-diameter CNTs exhibit negligible local curvature at the binding interface, GNR serves as a reasonable structural and electronic model. This substitution enables the precise evaluation of local interfacial chemistry, such as Al-O-C chemical anchoring, while significantly reducing the computational cost required to model a full CNT

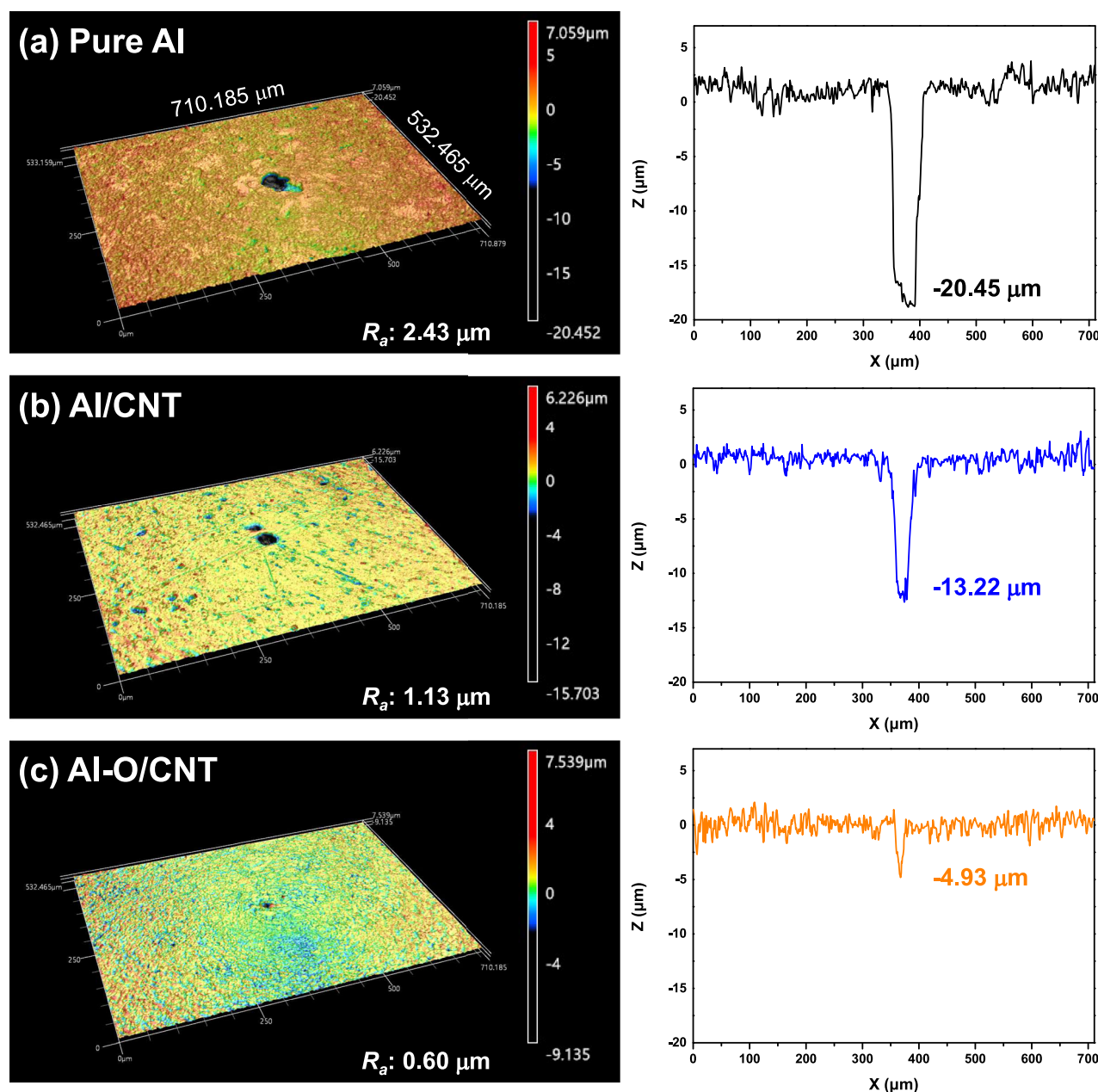


Fig. 3 | 3D Surface morphology and profile graph of specimens after spray test. a pure Al, b Al/CNT, and c Al-O/CNT.

within a periodic supercell^{22,23}. As shown in Fig. 7(a), the adsorption of GNR on the pristine Al surface yielded an adsorption energy of -3.52 eV at an equilibrium distance of approximately 3.2 Å. In contrast, for the Al-O surface, the adsorption distance decreased to approximately 3.0 Å, and the adsorption energy decreased to a significantly more negative value of -5.72 eV, indicating the formation of stable chemical anchoring (Fig. 7(b)). These calculated parameters for both the pristine Al and oxidized interfaces are highly consistent with previously reported values, confirming the reliability of our computational framework^{24,25}.

To elucidate the mechanism behind the enhanced GNR adsorption upon oxygen addition, electronic structure analyses were conducted. First, charge density difference (CDD) analysis was performed to examine the charge distribution in the Al/CNT and Al-O/CNT models. While the Al/CNT interface showed minimal charge redistribution, the Al-O/CNT interface exhibited significant charge transfer and redistribution between

the GNR and the Al-O slab (Fig. 7(c), Fig. S3). Furthermore, the projected density of states (PDOS) for GNR adsorbed on both Al and Al-O surfaces was analyzed (Fig. 7(d)). For the pristine Al surface, the overlap between the Al 3p and C 2p states was negligible at lower energy levels, indicating weak orbital hybridization. In contrast, on the Al-O surface, the bonding with oxygen shifted the Al 3p states to deeper energy levels, leading to a much stronger interaction with the C 2p orbitals of the GNR. These electronic structure findings consistently support the conclusion that the Al-O surface provides significantly enhanced adsorption for graphene compared to the pristine Al surface, primarily driven by the formation of robust Al-O-C chemical anchoring.

To evaluate the influence of the Al-O-C chemical anchoring on the mechanical stability and integrity of the composite interface, the work of adhesion (W_{ad}) was quantified using DFT calculations (Table 2). The W_{ad} serves as a key thermodynamic descriptor representing the intrinsic

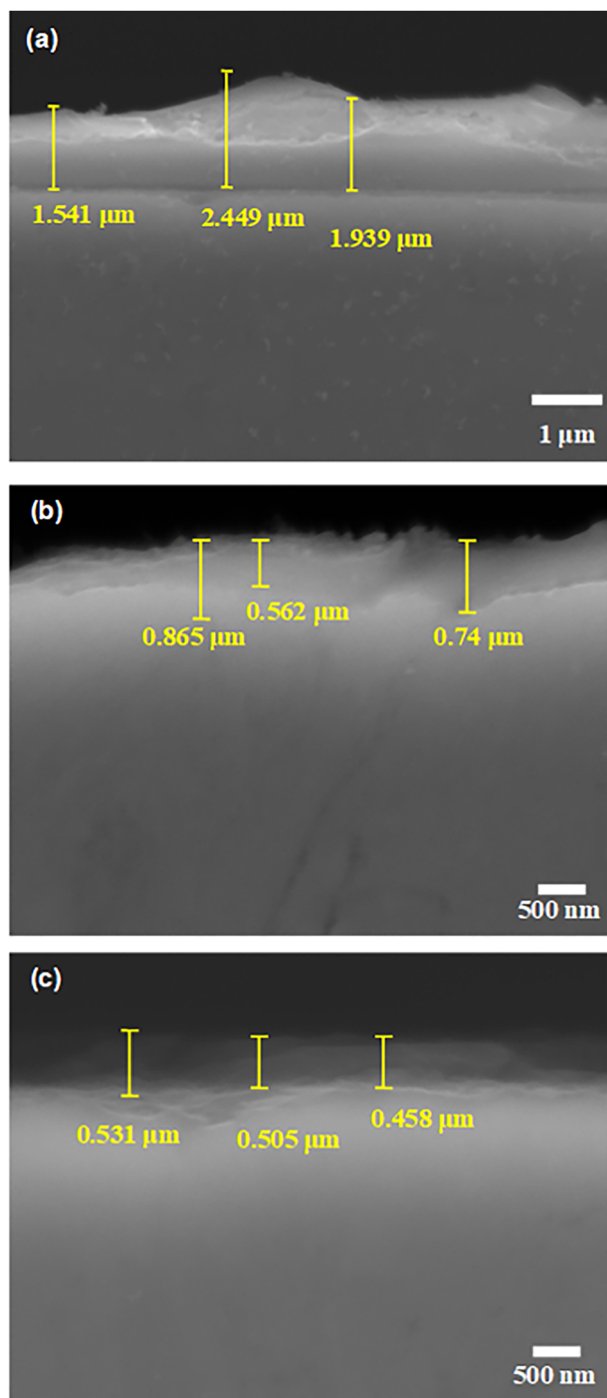


Fig. 4 | Cross-sections of corrosion morphologies of specimens after salt spraying. **a** pure Al, **(b)** Al/CNT, and **(c)** Al-O/CNT.

mechanical bonding strength and resistance to interfacial fracture²⁶. It was determined via the relation $W_{ad} = -E_{ads}/A$, where E_{ads} is the adsorption energy of the GNR on the substrate and A denotes the corresponding interfacial contact area. The calculated W_{ad} for the conventional Al/CNT interface is 0.72 J/m². In contrast, the interfacially engineered Al-O/CNT interface exhibits a significantly higher W_{ad} of 1.18 J/m², representing a 63% enhancement. This substantial increase in W_{ad} is closely correlated with the localized electronic structures; the oxygen bridge at the Al-O/CNT interface induces extensive interfacial charge transfer compared to the pristine Al/CNT system, as corroborated by the charge density difference analysis. This elevated structural and thermodynamic stability indicates that the dense Al-O-C chemical anchoring network can effectively withstand mechanical load

transfer without premature interfacial sliding or debonding. Consequently, the initiation of mechanical micro-cracks under stress is suppressed, effectively blocking the physical penetration pathways through which aggressive chloride ions could otherwise infiltrate.

These theoretical findings align well with previously reported experimental results on similar Al-O/CNT composites. A prior study reported that oxygen-mediated interfacial bonding between CNTs and the Al matrix led to enhancements in hardness, yield strength, and elastic modulus in Al-O/CNT composites compared to conventional Al/CNT counterparts²⁷. These observations demonstrate that oxygen-mediated interfacial engineering does not compromise the strength or stiffness of the composite, but rather contributes to strengthened interfacial bonding and improved load-transfer capability. This trend is highly consistent with our computational results, where the work of adhesion W_{ad} at the Al-O/CNT interface was found to be superior to that of the conventional Al/CNT interface. It should be noted, however, that the specific impacts on ductility and fracture toughness were not directly evaluated in the present study.

To further bridge these static thermodynamic findings with the macroscopic corrosion kinetics²⁸, the energetic landscape of chloride ion diffusion across the interface was investigated. The Gibbs free energy change for chloride adsorption (ΔG_{Cl^-}) was calculated at two distinct structural locations: on top of the GNR (top site) and intercalated within the interfacial gap between the GNR and the aluminum substrate (intercalated site), as illustrated in Fig. 7(e). For the conventional Al/CNT system, the adsorption energy at the intercalated site (+ 0.97 eV) is lower than that on the top site (+ 1.54 eV). This thermodynamic preference indicates that chloride ions can infiltrate into the weakly bonded interface with relatively low resistance, potentially accelerating localized corrosion kinetics. In stark contrast, for the interfacially engineered Al-O/CNT system, the internal intercalation of chloride incurs a substantial energetic penalty^{29,30}, raising the free energy to +3.54 eV compared to +2.17 eV at the top site. This significant energy landscape variation demonstrates that the inward migration of chloride ions into the interfacial gap is highly unfavorable. Consequently, the robust Al-O-C chemical anchoring network imposes a formidable energetic barrier that effectively suppresses the kinetics of chloride diffusion toward the underlying aluminum matrix, acting as a definitive chemical trap that corroborates the near-complete surface chloride localization observed in the XPS analysis.

The macroscopic stability observed in the cross-sectional analysis (Fig. 4) is intrinsically governed by the atomic-scale chemical environment at the interface, as revealed by the XPS bonding fractions (Fig. 6). The fundamental transition from a thick, porous Al(OH)₃ layer in pure Al to a thin, dense protective film in the Al-O/CNT composite can be explained through the dual role of the Al-O-C chemical anchor. First, the Al-O-C bridge acts as a thermodynamic stabilizer for the passive film, effectively suppressing the detrimental hydration process. According to the XPS results in Fig. 6d, the Al-O/CNT composite possesses the highest lattice oxygen (O²⁻) fraction of 19.21%, nearly double that of pure Al (10.91%). In conventional aluminum corrosion, the protective Al₂O₃ film readily reacts with water molecules to form voluminous Al(OH)₃, which lacks structural integrity and allows electrolyte ingress. However, the pre-existing Al-O-C chemical bridge—characterized by its high thermodynamic stability—anchors the oxygen atoms within the oxide lattice. This anchoring effect prevents the structural breakdown and hydration of the passive film, maintaining the integrity of the barrier layer and resulting in the exceptionally thin 0.45 μm corrosion layer observed in Fig. 4c. Second, the near-complete (99.8%) immobilization of metal chlorides in the Al-O/CNT composite provides a definitive chemical trap mechanism against chloride penetration. As shown in the Cl 2p spectra (Fig. 6c), while pure Al and Al/CNT exhibit significant fractions of organic/physisorbed chlorides (38.69% and 28.17%, respectively) which are prone to inward diffusion, the Al-O/CNT system captures chloride ions into stable metal-halide complexes at the very top of the interface. This high metal chloride fraction does not indicate severe corrosion; rather, it signifies that the aggressive Cl⁻ ions are effectively neutralized and fixed at the surface. By preventing these ions from reaching

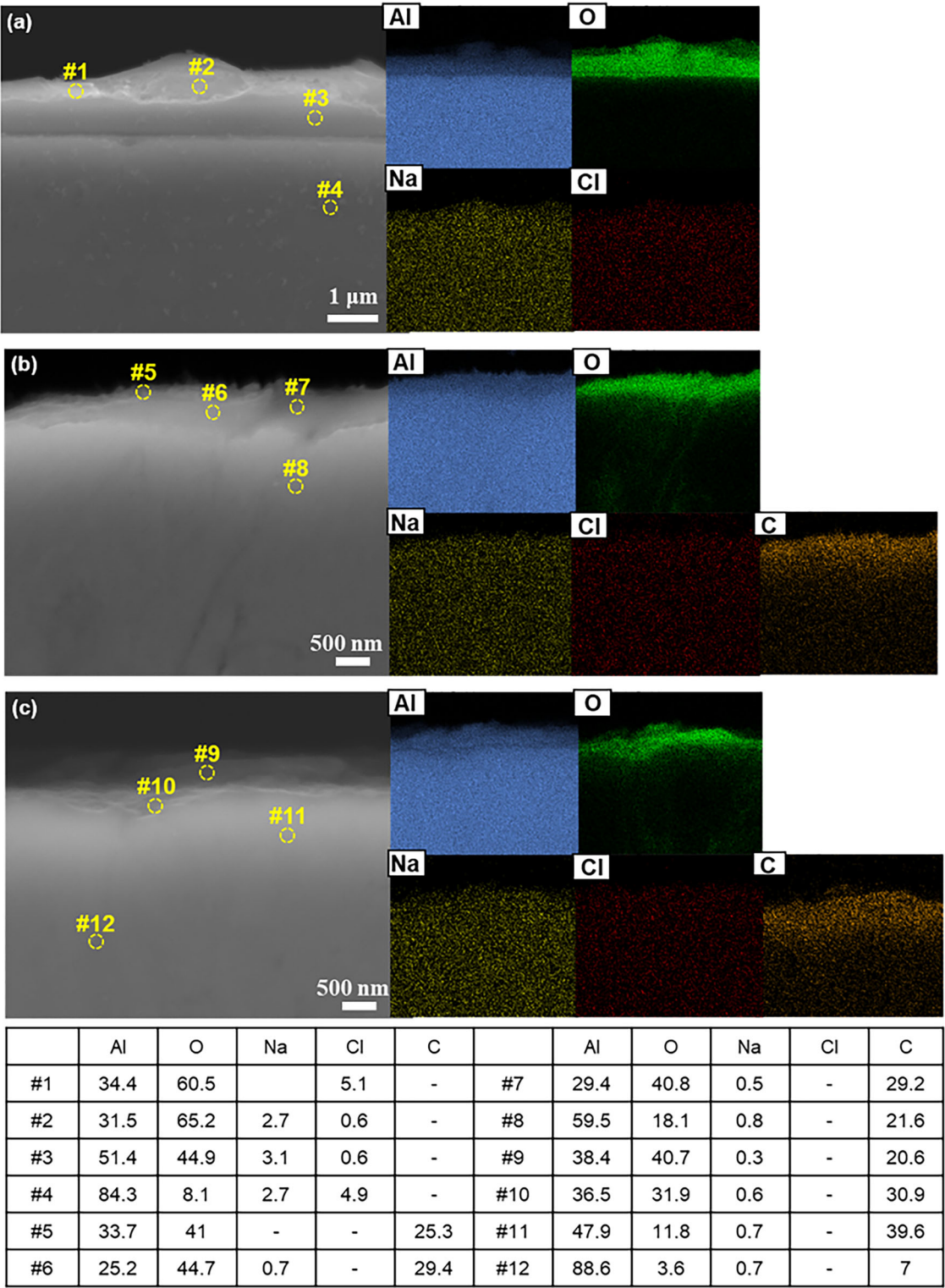


Fig. 5 | SEM morphologies and EDS compositions at the corrosion layer and interface of specimens after salt spray test. a pure Al, (b) Al/CNT, and (c) Al-O/CNT.

the Al matrix, the Al-O-C network seals the potential diffusion paths, a finding that perfectly aligns with the absence of chloride in the EDS maps of the Al-O/CNT interface (Fig. 4c).

In conclusion, the Al-O-C chemical anchoring establishes a superior multi-level defense system. By simultaneously stabilizing the O²⁻ lattice against hydration and trapping (or immobilizing) corrosive Cl⁻ ions at the surface, the engineered interface creates an impenetrable thermodynamic barrier. This synergistic mechanism, validated by the correlation between

the thinnest cross-section in Fig. 4 and the unique chemical signatures in Fig. 6, serves as the pioneering principle for the unprecedented corrosion resistance achieved in this study.

The unprecedented corrosion resistance achieved in the Al-O/CNT composite is the result of a synergistic multi-level defense system that operates across different length scales. At the microscopic scale, the physical barrier effect of the CNT network plays a primary role. The high aspect ratio and uniform distribution of CNTs create a tortuous path for corrosive

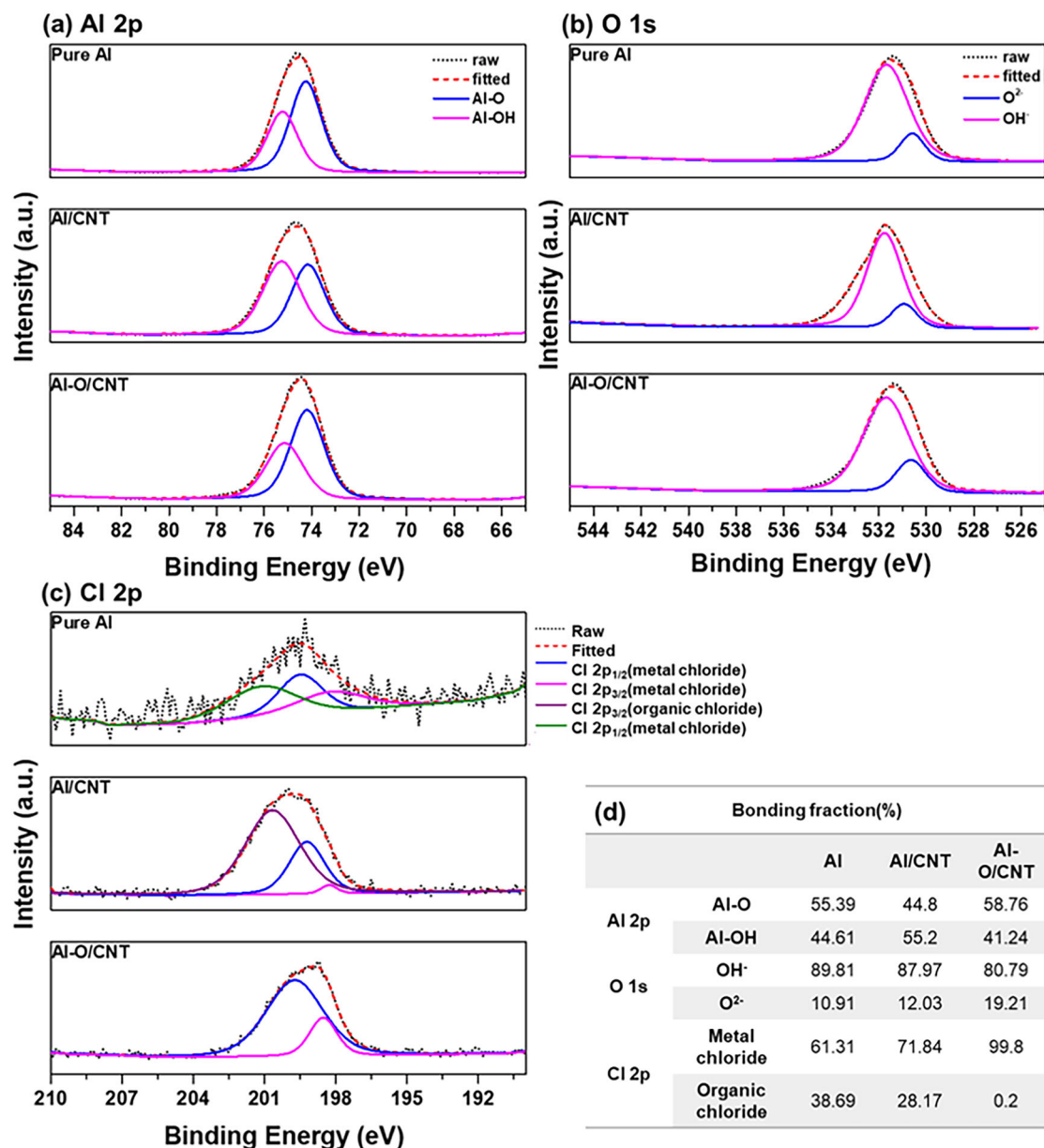


Fig. 6 | XPS spectra of corrosion samples of pure Al, Al-CNT, Al-O-CNT composites. **a** Al 2p, **b** O 1s, **c** Cl 2p and **d** bonding fractions.

electrolytes, effectively increasing the diffusion distance for Cl⁻ ions and oxygen molecules. This physical obstruction retards the initial onset of localized pitting, as evidenced by the reduced mass change in Table 1 compared to pure Al. However, as observed in the Al/CNT specimen, a physical barrier alone is insufficient to prevent atomic-scale degradation at the interface. The second, and more critical, level of defense is the atomic-scale chemical anchoring provided by the Al-O-C bridge. While the CNTs block the bulk ingress of the electrolyte, the Al-O-C bonds (−5.72 eV) establish an impenetrable thermodynamic seal at the Al matrix interface. This chemical anchor simultaneously stabilizes the O²⁻ lattice against hydration and traps Cl⁻ ions into stable metal-chloride complexes at the surface (99.8% anchoring). The integration of these two mechanisms—physical tortuosity and chemical anchoring—creates a synergistic shield that prevents the transition from a protective Al₂O₃ film to a voluminous, non-protective Al(OH)₃ layer. In this configuration, the dense interfacial oxide layer acts as a dielectric spacer, effectively decoupling the electrical continuity between the conductive CNTs and the Al matrix. By eliminating this electronic pathway, the CNTs are electrically isolated, thereby

suppressing the cathodic micro-galvanic reaction while simultaneously maintaining the physical ‘tortuous path’ that limits ion diffusion. This dual-action defense system is the fundamental reason why the Al-O/CNT composite maintains a stable corrosion layer of only 0.45 μm, establishing a new paradigm for the design of durable metal matrix composites.

In this study, we successfully engineered a highly corrosion-resistant Al-O/CNT composite by establishing a robust Al-O-C chemical anchoring at the interface. The key findings are summarized as follows:

- 1) The Al-O/CNT composite exhibited a remarkably low mass change (0.0028 g/cm²) and a significant noble shift in corrosion potential (E_{corr} = −0.75 V). SEM cross-sectional analysis confirmed that the Al-O/CNT system maintained an exceptionally thin and uniform corrosion layer of 0.45 μm, a four-fold reduction compared to pure Al (2.45 μm).
- 2) XPS analysis provided definitive evidence of the chemical anchoring mechanism. The Al-O-C bridge thermodynamically stabilized the lattice oxygen (O²⁻), suppressing the hydration of the passive film into Al(OH)₃. Furthermore, a near-complete (99.8%) anchoring of metal

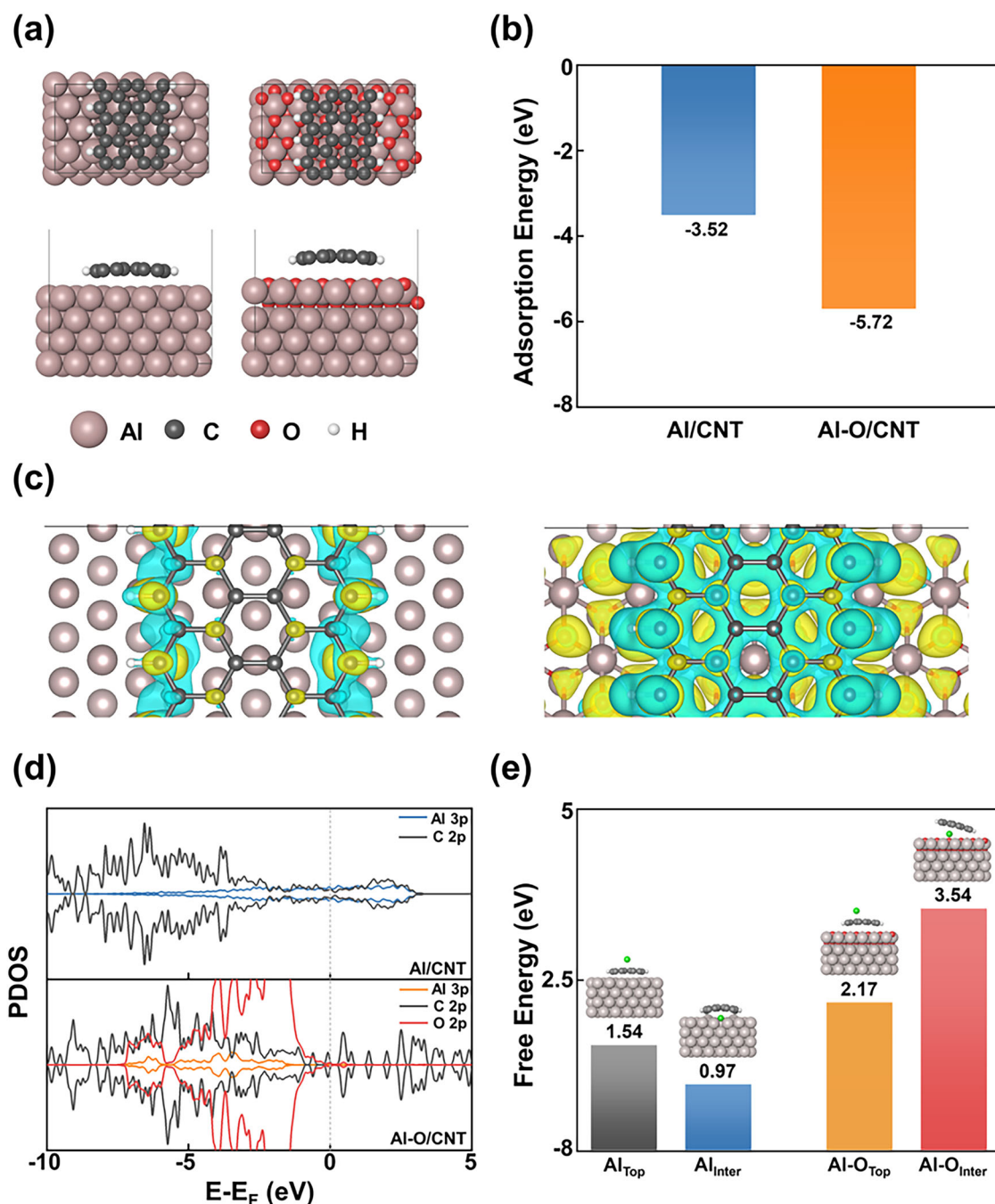


Fig. 7 | Density functional theory (DFT) evaluations of the interfacial chemical anchoring and thermodynamic resistance against chloride intercalation. **a** Top and side views of the optimized structures of Al/CNT and Al-O/CNT models. The coral brown, black, red and white spheres represent Al, C, O and H atoms, respectively. **b** Adsorption energy plot for CNT adsorption on Al and Al-O. **c** Top view of charge density difference of Al/CNT and Al-O/CNT. The charge accumulation and depletion regions are shown in yellow and cyan, respectively, with an isosurface level

of 0.001 e/Bohr³. **d** Projected density of states (PDOS) of the surface Al atoms and the C atoms of the adsorbed CNT in Al/CNT and Al-O/CNT. **e** Calculated Gibbs free energy of Cl adsorption at different structural sites within the Al/CNT and Al-O/CNT systems. The “Top” site refers to Cl adsorption on the upper surface of the GNR, while the “Inter” site indicates Cl intercalation between the GNR and the Al matrix.

- chlorides was achieved at the interface, effectively trapping corrosive Cl⁻ ions at the surface and preventing their inward diffusion.
- 3) DFT simulations corroborated the experimental observations, revealing a dramatic increase in interfacial stability as the binding energy shifted from -3.52 eV (mechanical interlocking) to -5.72 eV (chemical anchoring). This high bond energy functions as an electronic and thermodynamic barrier against electrolyte penetration.

- 4) The enhanced performance is attributed to a multi-level defense system where the physical tortuosity of the CNT network and the atomic-scale chemical anchoring of the Al-O-C bridge work in tandem to guarantee long-term surface passivity.

This research demonstrates that interfacial design via chemical anchoring is a critical strategy for overcoming the inherent electrochemical instability of metal matrix composites, providing a pioneering framework

Table 2 | Calculated adsorption energy (E_{ads}), interfacial contact area (A), and work of adhesion (W_{ad}) of the GNR in the Al/CNT and Al-O/CNT systems

	E_{ads} (eV)	A ($\text{\AA}^2$)	W_{ad} (J/m ^{2})
Al/CNT	−3.52	78.2	0.72
Al-O/CNT	−5.72	77.9	1.18

for developing advanced materials for high-durability applications. Our analysis reveals a crucial phenomenon, which is the Al-O-C anchored interface acts as a selective immobilization for chloride ions. While pure Al and Al/CNT allow chloride to penetrate deep into the matrix, the Al-O/CNT composite achieves a near-complete (99.8%) anchoring of metal chlorides directly at the stabilized interface. By capturing Cl^- ions at the surface and preventing their diffusion into the bulk, the Al-O-C anchor effectively halts the propagation of pitting. Furthermore, the increased fraction of lattice oxygen (O^{2-}) observed in Al-O/CNT (19.21%) compared to pure Al (10.91%) provides direct evidence that the chemical anchoring thermodynamically suppresses the detrimental hydration of the passive film into $\text{Al}(\text{OH})_3$.

Methods

Sample preparation

Three types of specimens, Pure Al, Al/CNT, and Al-O/CNT, were prepared for this study. The matrix materials utilized were aluminum powder (99.5% purity, diameter < 75 μm ; Al Co., Ltd., Japan) and Al-O powder (diameter 100–150 μm ; I-Al, Korea). Multi-walled carbon nanotubes (average diameter of 20 nm, length of 5 μm ; Applied Carbon Nano Technology Co., Ltd., Korea) were incorporated as the reinforcement at a fixed volume fraction of 3 vol%³¹. To achieve a uniform dispersion of CNTs, high-energy ball milling was employed for 12 h at a rotational speed of 500 rpm. The process was carried out using stainless steel balls (5 mm diameter) with a ball-to-powder weight ratio (BPR) of 15:1. To prevent atmospheric oxidation and excessive cold welding, the milling was conducted under a protective Argon (Ar) atmosphere with the addition of stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$) as a process control agent. Following the ball-milling process, approximately 10 g of the as-milled composite powder was charged into a hot-work tool steel (SKD61) mold with a diameter of 30 mm. The consolidation was subsequently carried out via a hot-pressing process under an ambient atmosphere at a sintering temperature of 450 °C and an applied axial pressure of 270 MPa for a dwelling time of 1 h. The resulting hot-pressed compacts were fabricated as disk-shaped specimens possessing a diameter of 30 mm and a thickness of approximately 5 mm.

Salt spray test and potentiodynamic polarization analysis

Salt spray testing was carried out on bare substrate, as-sprayed and heat-treated coatings using Atlas, USA, make CCX 2000 instrument. Bath conditions were maintained as per ASTM B117 standard with 5 wt.% NaCl solution. The salt spray tests were carried up to 48 h at 35 °C. To examine the oxide growth kinetics, the samples which are exposed to salt spray environment were taken out of the chamber at 48 h.

Potentiodynamic polarization measurements were carried out in a typical three-electrode cell setup with the specimen as a working electrode, a saturated calomel reference electrode (SCE), and a platinum counter electrode. The potentiodynamic polarization tests were performed in a 3.5 wt.% NaCl solution to simulate an aggressive marine environment. This electrochemical evaluation allowed for a comprehensive assessment of the corrosion behavior under conditions closely mimicking actual seawater exposure. The specimen was scanned potentiodynamically at a rate of 0.5 mV/s from the applied potential range of −0.5 to +1.5 V versus open circuit potential (OCP) to measure the anodic and cathodic current density changes.

DFT simulations

All spin-polarized Density Functional Theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP 5.4.4)^{32,33}. The exchange-correlation was treated within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional^{34,35}. The ion-electron interactions were described using the projector augmented-wave (PAW) method³⁶. The valence electron configurations for Al, O, C, and H were treated as $3s^2 3p^1$, $2s^2 2p^4$, $2s^2 2p^2$, and $1s^1$, respectively. To account for weak van der Waals interactions, Grimme's empirical dispersion correction (DFT-D3) was employed³⁷. A plane-wave cutoff energy of 500 eV was chosen. The electronic self-consistency convergence criterion and the force convergence criterion were set to 10^{-6} eV and 0.02 eV/ $\text{\AA}$, respectively. The Brillouin zone was sampled using Monkhorst-Pack³⁸ k-point meshes of $7 \times 7 \times 7$ for the bulk Al, $1 \times 3 \times 1$ for the isolated GNR, and $2 \times 3 \times 1$ for the all slab systems. For more accurate electronic structure analysis, a denser k-point mesh of $5 \times 5 \times 1$ was utilized. The Al bulk was modeled in a face-centered cubic (fcc) structure with the $Fm\bar{3}m$ space group. The Al(111) surface was modeled using a four-layer slab (Fig. S1(a)) because it is generally considered the most stable low-index surface of fcc aluminum due to its lowest surface energy³⁹. During the geometry relaxation, the bottom two layers were fixed to mimic bulk-like properties, while the top two layers and all adsorbates were fully relaxed. To construct the Al-O model, oxygen atoms were adsorbed at the hollow sites both above and below the topmost Al layer to represent an oxidized layer (Fig. S1(b)). A vacuum region of 20 $\text{\AA}$ was inserted along the z-direction to prevent periodic interactions. The GNR was modeled as periodic along the y-axis and hydrogen-terminated at the edges along the x-axis. To minimize self-interactions caused by periodic boundary conditions (PBC), the Al slab supercell was sufficiently expanded along the x-axis.

The adsorption energy (E_{ads}) of the GNR on the Al and Al-O slabs was calculated using the following Eq. (1):

$$E_{\text{ads}} = E_{\text{tot}} - E_{\text{slab}} - E_{\text{GNR}} \quad (1)$$

where E_{tot} , E_{slab} , and E_{GNR} denote the total energies of the GNR-adsorbed system, the clean slab (pristine Al or Al-O), and the isolated GNR, respectively.

Furthermore, the charge density difference ($\Delta\rho$) was calculated using Eq. (2) to investigate the charge transfer at the interface:

$$\Delta\rho = \rho_{\text{surf+GNR}^*} - \rho_{\text{surf}} - \rho_{\text{GNR}} \quad (2)$$

where $\rho_{\text{surf+GNR}^*}$, ρ_{surf} , and ρ_{GNR} represent the charge densities of the GNR-adsorbed surface, the clean surface, and the isolated GNR, respectively. The resulting three-dimensional charge density distributions were visualized using the VESTA software, with an isosurface level set to 0.001 e/Bohr^3 ⁴⁰.

Microstructural evaluation

Phase identification was performed by X-ray diffraction (XRD, D8 Discover, Bruker, USA) using a current of 40 mA and an accelerating voltage of 30 kV. Compositional analysis was conducted by energy-dispersive spectroscopy (EDS) attached to a scanning electron microscope (SEM, JSM-7100F, JEOL, Japan). The bonding states of both the composites with depth profiles were determined using X-ray photoelectron spectroscopy (XPS; K-alpha, Thermo VG, U.K.). The XPS analysis was performed using the Al K α line (1486.6 eV) for excitation, with measurements performed at resolutions of 50 and 0.1 eV energy steps. Depth profiling employed sequential 200 s sputter cycles to monitor binding energy variations as a function of depth. 3D laser microscopy (VK-X1050, KEYENCE, Japan) was used to perform three-dimensional surface analysis of the worn surfaces.

Data availability

The datasets generated and/or analysed during the current study are not publicly available due to institutional data management policies, but are available from the corresponding author on reasonable request.

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Author contributions

S.E.S. directed the research project. S.M.K. and S.Y.G. designed and produced the samples. J.B.H., B.H.K. and D.H.B. analyzed the data. All authors discussed and commented on the results.

Competing interests

The authors declare no competing interests.

Additional information

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