Corrosion Resistance of Sulfur–Selenium Alloy Coatings

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Despite decades of research, metallic corrosion remains a long-standing challenge in many engineering applications. Specifically, designing a material that can resist corrosion both in abiotic as well as biotic environments remains elusive. Here a lightweight sulfur–selenium (S–Se) alloy is designed with high stiffness and ductility that can serve as an excellent corrosion-resistant coating with protection efficiency of ≈99.9% for steel in a wide range of diverse environments. S–Se coated mild steel shows a corrosion rate that is 6–7 orders of magnitude lower than bare metal in abiotic (simulated seawater and sodium sulfate solution) and biotic (sulfate-reducing bacterial medium) environments. The coating is strongly adhesive, mechanically robust, and demonstrates excellent damage/deformation recovery properties, which provide the added advantage of significantly reducing the probability of a defect being generated and sustained in the coating, thus improving its longevity. The high corrosion resistance of the alloy is attributed in diverse environments to its semicrystalline, nonporous, antimicrobial, and viscoelastic nature with superior mechanical performance, enabling it to successfully block a variety of diffusing species.

1. Introduction

Corrosion has compromised structural materials since the dawn of human civilization. The annual direct cost of metallic corrosion is estimated to be ≈$300 billion in the United States and ≈€200 billion in Europe.[1] Steel is one of the most widely used alloys in production and manufacturing, utilities, transportation, defense, and infrastructure; however, it is susceptible to a diverse range of corrosive environments catalyzed by oxygen, moisture, electrolytes, and microbes.[2,3] It remains a long-standing challenge to develop a coating that can protect steel in both abiotic as well as biotic environments. For example, while inorganic coatings (e.g., zinc- and chromium-based) form an effective barrier against moisture and Cl\(^{-}\) ions, they do not work well against...
sulfate-reducing biofilms.\textsuperscript{[1,4]} Moreover, the utilization of such inorganic coatings is being increasingly restricted by governmental regulation because of their adverse effects on human health and the environment. Polymer-based coatings such as polyaniline, polyurethane, zeolite, and epoxy protect steel effectively under abiotic conditions;\textsuperscript{[5–9]} however, they are susceptible to hydrolysis in biotic environments that induce cracks and localized corrosion.\textsuperscript{[10]} This biotic corrosion arises from the organic components of polymer coatings which serve as preferential macronutrients for cell metabolism, thereby supporting microbial growth and subsequent microbial-induced corrosion. Antimicrobial properties can be imparted to polymer coatings by dispersing nanoparticles (TiO\textsubscript{2}, Ag) in the base matrix.\textsuperscript{[11,12]} While such antimicrobial coatings are beneficial for combating corrosion under abiotic/biotic conditions, the addition of nanoparticles based on noble metals significantly increases the cost of the polymer coating.

Another emerging strategy to develop combined abiotic and biotic corrosion resistive films is to use 2D coatings of layered graphene or hexagonal boron nitride.\textsuperscript{[13a–c–16]} Conformal coatings based on 2D materials and their heterostructures offer attractive routes to protect metals against aggressive environments including thermal oxidation, microbial corrosion, and atmospheric corrosion. However, complexity in the current nanomanufacturing methods and limited availability make it challenging to achieve defect (pinhole) free growth of 2D material coatings on large area surfaces.\textsuperscript{[17,18]} Irrespective of the coating material, defects in any coating can significantly influence the corrosion behavior and moderate the service life of the coated base materials. Therefore, there is an urgent need for an effective (both in defect free and defective condition) corrosion-resistant coating to protect metals such as steel from a diverse array of corrosive species, both under biotic and abiotic conditions.

Here we report an anticorrosive coating using a stable alloy comprised of two chalcogenides—sulfur and selenium (S–Se) that are cast as a conformal ductile coating on mild steel substrates. This S–Se alloy adheres well to steel, acts as a corrosion-resistant coating under both abiotic (simulated seawater and 0.1 m sodium sulfate salt media) and biotic (an aggressive sulfate-reducing bacterial medium) environments, is non-porous and does not dissolve in typical solvents including water, acetone, and isopropanol, making it an ideal anticorrosive coating for many disparate environments. Ab initio analyses of the interaction of the alloy with both the surface of steel and corrosion agents, confirm its excellent adhesion to the substrate and its superior resistance to various corrosion agents. As such, our results demonstrate that the as-produced S–Se coating shows outstanding potential as a high-performance and versatile barrier coating in a variety of corrosive environments. Additionally, the alloy coating possesses a remarkable ability to repair damage (e.g., pinholes) and recover the coating performance, which we attribute to its viscoelastic nature. Such phenomena provide the added advantage of significantly reducing the probability of a defect being generated and sustained in our coating, thus improving its longevity.

2. Results and Discussion

2.1. Fabrication, Structure, and Mechanical Property Profile

Sulfur-selenium (S–Se) alloy coatings were synthesized by mixing elemental sulfur and selenium in a 1:1 molar ratio and then heating to \textasciitilde300 °C in a ceramic mold placed inside a tube furnace in an inert argon atmosphere. Interestingly, the alloy behaves like an elastomeric polymer, where it undergoes high deformation upon compressive loading and recovers its original shape upon removal of load at room temperature.\textsuperscript{[21]} Furthermore, this material exhibits a temperature-dependent viscosity (Figure S1a, Supporting Information). As the temperature of S–Se is increased from \textasciitilde100 to \textasciitilde180 °C, the viscosity is reduced by about three orders of magnitude. We identified the most suitable temperature (\textasciitilde130 °C) for coating based on the viscosity or flowability of the alloy. Thin coatings of the alloy were obtained by using a handmade doctor blade method where S–Se was kept on a hotplate at \textasciitilde130 °C and coated onto a mild steel (MS, AISIS 1018) coupon (Figure 1a). After coating, the S–Se/MS was placed at room temperature immediately to prevent the accumulation of the S–Se alloy owing to its high viscosity. The average thickness of the coating, as observed from the cross-sectional scanning electron microscope (SEM) images was determined to be \textasciitilde100 µm. (Figure 1b). After the coating was prepared, the structure was analyzed using X-Ray diffraction (XRD). XRD confirmed the semicrystalline nature of the S–Se coating (Figure 1c). The crystalline peaks indexed in XRD corresponds to monoclinic S–Se (blue ink) and hexagonal Se (black ink), respectively whereas the amorphous background signature indicated its amorphous nature.

Next, we investigated tribological properties by friction force microscopy (FFM) to understand the frictional behavior of S–Se/MS and bare MS samples as a function of applied normal load (Figure 1d; Figure S2, Supporting Information). Friction was higher overall for the S–Se coating than for bare MS and both experienced a friction increase as the normal load increased. Additionally, both exhibit humidity-independent friction responses, suggesting a weak interaction of water with the S–Se surface (Figure S3, Supporting Information). Further, a nano-scratch test was carried out by applying a constant normal load (\textasciitilde3 mN) while measuring the force required to move the nanoindenter tip laterally by 10 µm. The scratch steadily deepened due...
to increasing normal load resulting in material pile-up at the end of scratch, with negligible side build-up (Figure 1e). The maximum lateral force experienced by the indenter was approximately 1.35 mN (Figure S4, Supporting Information), which is significantly higher than what has been reported for polymer nanocomposite based anticorrosion coatings.[24] This indicates that the S–Se coating has high wear resistance because it resists scratching, which is reflected in the larger lateral indenter force. We also determined the coefficient of friction (ratio of lateral to normal force) of the S–Se alloy to be $\approx 0.45$, which indicates that the S–Se coating exhibits high wear-resistance.

After tribological analysis, we conducted adhesion studies of the S–Se coating onto mild steel surfaces to ensure that delamination would not be a concern under normal operating conditions. Using the pull-off test technique, in which flat counter surfaces were attached onto the coating with epoxy and pulled using a force gauge, we observed cohesive failure with an average cohesion of $0.37 \pm 0.18$ MPa (Figure S5, Supporting Information). This demonstrates that the coating-steel bond is stronger than the mechanical cohesion within the coating. These results indicate good adhesion properties between the S–Se/MS and that failure would likely be cohesive in nature for the coating.

Next, we conducted a nanoindentation test to understand the elastic and plastic behavior of the S–Se coating. From the load-displacement curve (Figure 1f), the hardness and reduced moduli of the coating were calculated to be $426$ MPa and $8.08$ GPa, respectively by the Oliver and Pharr method.[25] It can be inferred from the mapping data that the coating is homogenous over the substrate and the mechanical properties are in line with the single indentation results (Figure S6 and Table S1, Supporting Information). The value of the plasticity index (i.e., the ratio of the area enclosed between loading–unloading
curves to the area under the loading part of the curve) for S–Se alloy is found to be ≈0.6, which is comparable to commercial polymer coatings such as epoxy, polycarbonate, poly (methyl methacrylate), and ultrahigh molecular weight polyethylene. While most of these polymers have moduli in the range of 0.5–5 GPa and hardness in the range of 0.1–0.3 GPa in nanoindentation experiments, S–Se exhibits markedly higher modulus (=8 GPa) and hardness (=0.43 GPa), while maintaining the plasticity index or ductile nature in the range observed for viscoelastic polymers (Figure 1g). The S–Se alloy developed in this work also exceeds the mechanical properties of polymer nanocomposites which incorporate nanoscale fillers, such as carbon nanotubes.[21] Additionally, while some inorganic coatings such as h-BN and fused silica have higher modulus and hardness, they lack the flexibility or ductility of the S–Se alloy. In addition, thermogravimetric analysis (Figure S1b, Supporting Information) also indicated high temperature stability of the S–Se alloy. Thus, the unique combinations of tribological, mechanical, and thermal properties displayed by the S–Se alloy makes it a superior coating when compared to current state-of-the-art anticorrosive materials.

2.2. Corrosion Resistance in Abiotic Environments

A promising application of the synthesized S–Se alloy is its use as an oxidation-resistant coating for steel surfaces in marine environments. To study its corrosion protection ability, S–Se/MS along with bare MS samples were exposed to simulated seawater containing 3.5% or 0.6 m NaCl for ≈30 d, which typically is more aggressive compared to natural seawater. The S–Se/MS sample did not exhibit any discoloration or change after 30 d, but the bare MS corroded significantly (visible as yellow stains in the optical image—Figure 2a). Further, the S–Se/MS sample

![Figure 2](image-url). Corrosion resistance of S–Se coating in abiotic environment (simulated seawater, i.e., 0.6 m NaCl). a) Mild Steel (MS) in simulated seawater after day 1 and day 30. The yellow residue in the water is a result of rust formation. Rust is also evident in the formation of brown lines on the MS surface. b) S–Se coated MS (S–Se/MS) in seawater on day 1 and day 30. No indication of coating detachment was observed in the residual seawater solution. c) Pristine bare MS before and after electrochemical destructive test in seawater. d) S–Se/MS before and after the electrochemical destructive test in seawater. The surface of S–Se/MS does not show any signs of deterioration while bare MS shows extensive rust formation. e–i) Destructive electrochemical test results after ≈50 min. of immersion in seawater. e) Potentiodynamic polarization (Tafel) plots. f) Cyclic voltammetry measurements. g) Bode magnitude and phase angle plots. EDS map showing the chemical composition of corrosion products for h) bare MS and i) S–Se/MS after exposure to simulated seawater. The S–Se/MS does not exhibit the presence of Fe element indicating barrier protection against electrochemical oxidation.
did not leave any residual S–Se flakes over a period of 30 d, indicating that the S–Se/MS interface is qualitatively stable and oxidation-resistant (Figure 2b). To study the corrosion kinetics of S–Se/MS in simulated seawater, accelerated electrochemical corrosion tests were performed to mimic the effects of aggressive species (chloride and oxygen) that are known to promote cathodic (oxygen reduction) and anodic (Fe oxidation) reactions and accelerate the corrosion of MS. Postmortem analysis of the degree of corrosion was performed using optical imaging. The optical images of bare MS (Figure 2c) show a high degree of corrosion attack with a rough (heterogeneous) surface having brown corrosion deposits indicating the formation of rust (i.e., iron oxide-hydroxide), whereas the S–Se/MS (Figure 2d) stayed intact with no signs of coating deterioration. We quantitatively analyzed the corrosion resistance of the S–Se/MS using potentiodynamic polarization (PDP) and cyclic voltammetry (CV) techniques. The PDP analysis showed that the S–Se coating suppressed corrosion rates by six orders of magnitude as compared to bare MS (Figure 2e; Table S2, Supporting Information). Further, the PDP or Tafel plots show larger open circuit potential (OCP) value (+363 mV) and significantly lower currents for S–Se/MS compared to bare MS (~657 mV), confirming the passivation behavior of the coatings against corrosive chloride attack. The CV measurements elucidate the impact of the coating as a barrier to chemical reactions involved in a corrosion process. The bare MS showed anodic (~0.70 V vs Ag/AgCl) and cathodic peaks (~1.71 V vs Ag/AgCl) with a sharp increase in corrosion current indicating electrodissolution of iron (Fe) ions (Figure 2f). In contrast, S–Se/MS showed a flat line even after 4 CV runs, clearly indicating a robust barrier between the electrolyte and MS, thereby preventing corrosion caused by aggressive chloride ions.

Electrochemical impedance spectroscopy (EIS) corroborated the strong corrosion barrier properties of the S–Se coating against simulated seawater (Figure 2g). In the low frequency (0.01 Hz) region of the Bode impedance plot, S–Se coatings exhibit seven orders of magnitude higher corrosion resistance (~15 160 MΩ cm²) than bare MS (~1.2 kΩ cm²). Note that, the corrosion resistance of the coating (Rcorr) was obtained by fitting the Bode plot to an electrical equivalent circuit (Figure S13c, Supporting Information). The phase angle plot for S–Se/MS shows two distinct phase angle peaks, with the first peak representing resistance to penetration of chloride ions through the coating at the electrolyte/coating interface and the second peak attributed to resistance to the electrochemical reaction at the electrolyte/substrate interface. The higher value of phase angle (~90°) at the middle (10 Hz) and high frequency (100 kHz) confirm the absence of electrochemical reactions at the S–Se/MS interface. In contrast, we observed low phase angle maxima (~50°) with a shift to the lower frequency for bare MS. The higher phase angle and impedance values for S–Se/MS denote a robust coating that lowers the corrosion reaction rates on the surface.

The signatures of corrosion attack by chlorides investigated using energy dispersive spectroscopy (EDS) analysis reveal the presence of Fe and O peaks on the bare MS surface (Figure 2h), suggesting the formation of iron-based corrosion products. The absence of these peaks on the S–Se/MS sample (Figure 2i) provides clear evidence that S–Se coatings suppress Fe dissolution. Additionally, we also conducted electrochemical corrosion analysis in aerated 0.1 M Na2SO4 salt solution to understand the corrosion resistance properties of S–Se alloy against sulfate salts. The corrosion resistance on S–Se/MS in sulfate medium was six orders of magnitude higher compared to the bare MS (Figures S7 and S8 and Table S3, Supporting Information). Thus, both the results in chloride and sulfate media demonstrate that S–Se alloy coatings are highly effective in combating corrosion in abiotic chemical environments.

2.3. Corrosion Resistance in Biotic Environments

After evaluating the protection of S–Se coatings in abiotic environments, we analyzed the ability of S–Se to suppress aggressive microbially induced corrosion (MIC) involving sulfate-reducing bacteria (SRB) “Desulfovibrio alaskensis G20” under anaerobic conditions. We evaluated the coating performance in both planktonic (SRB cells are in suspension for 2 h) and sessile forms (SRB cells are given 30 d to grow biofilms that are attached to the MS surface).

Tafel analysis and EIS were used to determine the performance of the S–Se coating exposed to planktonic cells within two hours of exposure. The results obtained from Tafel analysis (Figure 3a) show that the S–Se coating drastically decreases Fe dissolution due to biogenic H2S by SRB. The corrosion potential (Ecorr) for S–Se/MS is significantly larger (~280 mV vs ~647 mV for bare MS), and its current density (icorr) is seven orders of magnitude lower, compared to bare MS (Table S4, Supporting Information). The more positive potential and lower current density of S–Se is a signature of the effective inhibition by the coating against corrosive metabolites (H2S) associated with sulfate reduction. We calculated the inhibiting efficiency (η) of the S–Se coating to be ~99.99%. The corrosion rate for S–Se/MS (~2.24 × 10⁻⁴ mpy) was five orders of magnitude lower than bare MS (~15.5 mpy). Additionally, Bode magnitude and phase angle plots obtained from the EIS analysis (Figure 3b) confirm the barrier property of the coating. The S–Se/MS exposed to planktonic SRB showed six orders of magnitude higher impedance modulus values compared to bare MS in the low-frequency region (~0.01 Hz), while the phase angle for S–Se/MS was almost 90° in the high-frequency region (10⁵ Hz), in contrast to bare MS. As such, S–Se coatings are highly effective as anodic barriers to the underlying Fe surface, preventing oxidation kinetics under biotic planktonic conditions.

Compared to planktonic cells, sessile bacteria present in biofilms are known to accelerate corrosion rates by ~100-fold. After establishing the corrosion resistance of S–Se alloy against MIC by the planktonic cells, we further analyzed the corrosion behavior under sessile conditions over 30-d exposure time. Open circuit potential (OCP) for S–Se/MS (Figure 3c) is larger (more positive) compared to bare MS throughout the exposure time. For example, the OCP for S–Se/MS on day 1, 12, and 30 was 300, 140, and 112 mV higher compared to bare MS. To quantify the corrosion kinetics on a temporal scale, we used the linear polarization resistance (LPR) method. The corrosion rates obtained from LPR were consistent with the OCP trends. The corrosion rate (maximum value) recorded for S–Se/MS (0.04 mpy on day 30) was 1000 times lower compared to the
maximum corrosion rate for bare MS (43.97 mpy on day 30) (Figure 3d). As such, the S–Se coating acts as a protective layer and inhibits electrochemical reactions in sessile conditions also. EIS measurements corroborates the strong corrosion barrier properties of the coatings against SRB biofilms (Figure 3e). The low frequency (0.01 Hz) corrosion resistance obtained from the Bode plot of S–Se/MS on day 1 is four orders of magnitude higher (10^8 Ω cm^2) compared to bare MS (10^4 Ω cm^2). Similarly, on day 30, the corrosion resistance of S–Se/MS was 1000-fold higher compared to bare MS (Figure 3f). To observe biofilm growth and assess the degree of MIC resistance, the S–Se/MS and bare MS were removed from the corrosion cell after 30 d of exposure and analyzed using SEM, EDS, and XRD. SEM images of S–Se/MS and bare MS (Figure 3g.h; Figure S9, Supporting Information) clearly indicate that the S–Se coating discourages cell adhesion. The bare MS surface had more densely packed SRB cells, while the S–Se/MS surface contained very few SRB cells in an extracellular polymeric substance (EPS) matrix. Further, the biofilm matrix was analyzed for the possible formation of corrosion products. The XRD results revealed the presence of different phases of iron oxide, hydroxide and iron sulfide on bare MS (Figure S10, Supporting Information). In contrast, the S–Se/MS surface did not show any peaks for iron sulfide.

2.4. Comparative Studies with Commercial Coating

We assessed the performance of S–Se with commercial Zn coatings on mild steel (MS) substrates both in biotic and abiotic environments, having similar coating thicknesses (80–100 µm). Since the presence of defects in corrosion resistant coatings is a critical issue, we repeated the corrosion tests on pristine S–Se and Zn coatings as well as those with pin-hole defects. Results revealed that the pristine and defective S–Se coating on mild steel showed lower corrosion rates than pristine and defective Zn coating on mild steel respectively in both conditions (Figures S11 and S12; Tables S5–S8, Supporting Information). Additionally, we performed biotic and abiotic corrosion studies on a commercial epoxy coating (EPON 828, Hexion) with similar thickness as the S–Se alloy and observed higher performance for the later in both cases (Figures S13 and S14 and Tables S9 and S10, Supporting Information).

2.5. Corrosion Resistance Mechanism of the Alloy

To understand the corrosion mechanism of the S–Se coating, atomic scale density functional theory (DFT) simulations
were performed to understand the molecular unit interaction between mild steel, S–Se alloy and corrosion agents (O₂, OH⁻, HS⁻, H₂O, NaCl, Na₂SO₄). Our previous study has shown, through theoretical and experimental infrared and Raman spectra, that the perpendicular orientation between octa-sulfur and octa-selenium (S₈Se₈) depicted in Figure 4 is the likeliest unit for the S–Se alloy. There is a very strong dipolar attraction between S and Se, resulting in its insulating nature and high dielectric properties. Further, the mild steel used in our experiments contains a very low percentage of carbon atoms which makes it safe to assume that most of the interaction with the S–Se alloy at the interface happens with iron. Our computational model builds on these assumptions by simulating the interaction between the sulfur-selenium molecular unit (S₈Se₈) and Fe₂ in order to shed light on the chemical nature of the coating properties. We simulated the interaction between the sulfur-selenium unit and corrosive agents such as O₂, OH⁻, HS⁻, H₂O, NaCl, and Na₂SO₄ to examine the extent to which a significant degradation of the alloy ensues. We positioned Fe₂ and corrosion agents in the proximity of sulfur and selenium atoms to form several configurations and the most energetically favorable configurations were extracted for the computation of Gibbs free energies (Figure 4a–g). The difference in Gibbs free energy between products (Fe₂-S₈Se₈, O₂-S₈Se₈, OH⁻-S₈Se₈, HS⁻-S₈Se₈, H₂O-S₈Se₈, NaCl-S₈Se₈, Na₂SO₄-S₈Se₈) and respective reactants taken separately were more favorable for Fe₂-S₈Se₈ than for O₂-S₈Se₈, OH⁻-S₈Se₈, HS⁻-S₈Se₈, H₂O-S₈Se₈, NaCl-S₈Se₈, Na₂SO₄-S₈Se₈ (−2.422 Hartrees vs −2.040 Hartrees, −2.179 Hartrees, −2.095 Hartrees, −2.035 Hartrees, −2.197 Hartrees, −1.216 Hartrees, respectively). This means that the alloy forms stronger bonds with the reconstructed surface of mild steel than it does with corrosion agents. Except for sodium sulfate (Na₂SO₄), water (H₂O) appears to be the least corrosive of the corrosion agents because it has the second highest free energy difference between the products and reactants (−2.035 Hartrees). Bisulfide (HS⁻) thus appears to be one of the most corrosive of the corrosion agents (free energy difference −2.095 Hartrees) in accordance with its well-known highly toxic and corrosive properties. The validity of these conclusions is given by the fact that within the small size of our molecular model, the room-temperature equilibrium constant (exp(−ΔG/RT) with R being the universal gas constant) for the alloy-and-mild steel reaction was calculated to be ≈1.317 and that of the alloy-sodium chloride reaction (the best case among corrosion agents) was
calculated to be \(\approx 1.284\). This amounts to the forward reaction being roughly 2.59% more thermodynamically favorable with mild steel than with sodium chloride, which is already significant at the level of a single molecule and is expected to be quantitatively even more significant at the level of the bulk. It is also worth noting that the geometry of the molecular unit for S–Se is highly disrupted when interacting with \(\text{Fe}_2\) (Figure 4a). Indeed, \(\text{Fe}_2\) breaks both the S ring and the Se ring to form a highly disordered \(\text{Fe}_2\text{S}_x\text{Se}_y\) cluster, in agreement with the experimentally observed amorphous layer at the interface between the alloy and the surface of mild steel. In a diametrically opposite manner, the geometry of the molecular unit for the alloy is not disrupted when interacting with corrosion agents \(\text{O}_2\), \(\text{OH}^-\), \(\text{HS}^-\), \(\text{H}_2\text{O}\), \(\text{NaCl}\), \(\text{Na}_2\text{SO}_4\) (Figure 4b–g). Two observations are worth underscoring here. First, the ring-like structure of the alloy unit as well as the perpendicular orientation of the S ring and the Se ring are not significantly altered as a result of the interaction with the corrosive agents. Second, no intercalation of the corrosive agents into the S ring or the Se ring is observed. This is especially true for sodium sulfate that exhibits the highest free energy difference (\(\approx 1.216\) Hartrees). These two observations shed light on the chemical nature of the protective anticorrosive properties of the S–Se alloy and indicate that it is highly unfavorable for corrosion agents to permeate through the alloy units. Taken together, our simulations illustrate from a molecular perspective, two distinct behaviors of the alloy. On one hand, the alloy shows strong adhesion to the surface of mild steel, thus demonstrating its coating capabilities. On the other hand, the alloy exhibits outstanding resistance to corrosive agents thus demonstrating its anticorrosive properties.

Beside DFT simulations, we have experimentally analyzed the morphology of the S–Se coating to understand the corrosion protection mechanism. We analyzed the morphology of S–Se alloy using SEM to determine the porosity in the surface, since porosity will have an adverse effect on the ability of the film to block the penetration of corrosive species. The in-plane SEM images of S–Se alloy show a micro-scale uneven surface, although it appears flat from the macroscopic scale (Figure 4h). However, even at the highest magnification, there is no indication of any porosity present in the structure; thus, validating the previous ab initio calculations. Similarly, we did not observe any signs of porosity in the cross-section images either (Figure 4i). Besides our microscopic observations, we determined the pure-gas permeability of \(\text{He}, \text{N}_2, \text{CO}_2\), and \(\text{C}_2\text{H}_6\) at 35 °C and 2 bar through the S–Se alloy film (85 μm) (Figure 4j). Pure-gas permeability was found to be independent of the feed pressure, suggesting that the alloy films were defect-free. Helium exhibits a permeability as low as \(4.0 \times 10^{-11}\) mol m\(^{-1}\) s\(^{-1}\) bar\(^{-1}\) (or 1.2 Barrer), lower than most of the polymers and inorganic materials. Furthermore, the S–Se alloy shows a \(\text{CO}_2\) permeability of 0.27 Barrer, lower than that of conventional barrier materials,\(^{[29]}\) suggesting superior barrier properties for the S–Se alloy. It should be noted that increasing the penetrant size (as indicated by the critical volume) decreases the gas permeability through the S–Se alloy. Finally, XRD revealed our coating as a film and cut into two separate portions, the separated parts were found to be joined as a single piece when they were placed close to one another on a hotplate at a temperature near 70 °C (Figure 5c). This suggests that in the event of extreme mechanical loading, abrasion or wear, the damaged coating can be recovered without any additional expensive operations. It should be noted that one of the existing challenges with all corrosion resistant coatings is that they are essentially barrier coatings, with no ability to protect the substrate where they are not present. We envision that the S–Se alloy’s ability to recover mechanical damage and defects can significantly aid in combating corrosion under extreme circumstances. Additionally, we performed an atomic force microscopy (AFM) based scratch test and analysis on the S–Se coating for gaining further insight into its mechanical response. At first, a rectangular region of the alloy was scanned in contact mode with a high contact stress (\(\approx 1.5\) GPa), which resulted in surface dents, as seen in Figure 5a (0 min). After the contact mode scan, a larger area around the pre-scanned region was continuously scanned for one hour in tapping mode to avoid any sample damage,\(^{[20]}\) which reveals almost complete recovery of the topography. Figure 5b shows the time evolution of the coating morphology when scribed (scanned) with an AFM probe. As can be seen, the initial dents of \(\approx 250\) nm are almost completely recovered, rendering a nearly flat surface, within an hour of performing the initial scanning (scratching). These experimental observations demonstrate that the material is viscoelastic in nature, can dissipate energy during mechanical loading and/or impact and can gradually recover to its original state. This is further corroborated by the hysteresis observed in the load-displacement behavior from the nanoindentation test shown in Figure 6. Such viscoelastic recovery phenomena provide the added advantage of significantly reducing the probability of a defect being generated and sustained in our coating, thus improving its longevity. With a better understanding of the macroscopic and nanoscopic behavior of the alloy under mechanical deformation and damage, we conducted corrosion tests on the healed coating and the outcomes of the tests were similar to

We also performed antibacterial activity studies to understand the nature of the behavior of the S–Se alloy in biotic environments. Both S and Se have anti-bacterial and anti-microbial properties. Hence, the S–Se alloy is also likely to have antibacterial properties. The antibacterial activity of sulfur–selenium alloy against \(D. alaskensis\) was assessed using the bacterial plate count method on lactate C medium agar plates. The results showed that the percent reduction of \(D. alaskensis\) cells increased with increasing concentrations of S–Se (Figure 4k). \(D. alaskensis\) cells treated with 1 mg mL\(^{-1}\) showed the maximum percent reduction of 70%, followed by 0.75 mg mL\(^{-1}\), which showed a 39.8% reduction. This confirms that the S–Se alloy exhibits significant antibacterial activity, which explains its potency (see Figure 3) in suppressing biofilm formation and in preventing microbial corrosion in biotic environments.

2.6. Damage/Deformation Recovery Mechanism of the Alloy

Finally, we discovered an interesting mechanical response of the S–Se alloy. When the alloy was taken from the steel foil as a film and cut into two separate portions, the separated parts were found to be joined as a single piece when they were placed close to one another on a hotplate at a temperature near 70 °C (Figure 5c). This suggests that in the event of extreme mechanical loading, abrasion or wear, the damaged coating can be recovered without any additional expensive operations. It should be noted that one of the existing challenges with all corrosion resistant coatings is that they are essentially barrier coatings, with no ability to protect the substrate where they are not present. We envision that the S–Se alloy’s ability to recover mechanical damage and defects can significantly aid in combating corrosion under extreme circumstances. Additionally, we performed an atomic force microscopy (AFM) based scratch test and analysis on the S–Se coating for gaining further insight into its mechanical response. At first, a rectangular region of the alloy was scanned in contact mode with a high contact stress (\(\approx 1.5\) GPa), which resulted in surface dents, as seen in Figure 5a (0 min). After the contact mode scan, a larger area around the pre-scanned region was continuously scanned for one hour in tapping mode to avoid any sample damage,\(^{[20]}\) which reveals almost complete recovery of the topography. Figure 5b shows the time evolution of the coating morphology when scribed (scanned) with an AFM probe. As can be seen, the initial dents of \(\approx 250\) nm are almost completely recovered, rendering a nearly flat surface, within an hour of performing the initial scanning (scratching). These experimental observations demonstrate that the material is viscoelastic in nature, can dissipate energy during mechanical loading and/or impact and can gradually recover to its original state. This is further corroborated by the hysteresis observed in the load-displacement behavior from the nanoindentation test shown in Figure 6. Such viscoelastic recovery phenomena provide the added advantage of significantly reducing the probability of a defect being generated and sustained in our coating, thus improving its longevity. With a better understanding of the macroscopic and nanoscopic behavior of the alloy under mechanical deformation and damage, we conducted corrosion tests on the healed coating and the outcomes of the tests were similar to...
those performed on the pristine S–Se coating, highlighting the robustness and effectiveness of the anti-corrosive coating. S–Se coatings on MS were made defective by introducing identical pin-hole defects using a milling machine. Comparative Tafel plots (Figure 5d) show significantly lower currents in pristine S–Se/MS, followed by the healed S–Se/MS coating, in turn followed by the defective S–Se/MS, when exposed to *D. alaskensis* G20. On the other hand, in the abiotic environment (0.6 m NaCl), the Tafel plots (Figure 5e) show significantly lower currents in healed S–Se/MS, which behaves similar to pristine S–Se/MS, when compared to defective S–Se/MS. Details of these corrosion test results can be found in Tables S11 and S12 in the Supporting Information. This suggests that the defective S–Se/MS coatings, upon recovery, could potentially revert to their original excellent corrosion barrier properties.

### 3. Conclusion

In summary, unwanted metal corrosion costs industries across the world billions of dollars annually, and researchers have sought materials and methods to combat this issue for decades. However, many current advancements in anticorrosive coatings include prohibitively expensive materials or non-scalable processing methods that are not versatile enough to prevent corrosion in many different environments. In this study, we demonstrate S–Se alloy as a universal anti-corrosive coating, which is easily processed, mechanically robust, and effective in both biotic and abiotic environments. The S–Se coating displays moduli and hardness values far greater than most polymer and nanocomposite coatings, while also maintaining its ductile and elastic recovery nature, unlike inorganic coatings. S–Se alloy coatings are able to protect mild steel from diverse corrosive environments due to their unique combination of properties, which includes their insulating and impermeable nature, high coating capacitance, viscoelastic nature, and intrinsic antimicrobial properties. The coating also exhibits the ability to recover defects and damage with minimal intervention, and the recovered coating can effectively combat corrosion. We believe this study represents an important contribution to current high-performance coatings research field as a robust “all-in-one” anti-corrosion coating.

### 4. Experimental Section

Experimental section is provided in the Supplementary Information.[30–39]

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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[1] S. Böhm, Nat. Nanotechnol. 2014, 9, 741.
[2] R. E. Melchers, Bioelectrochemistry 2014, 97, 89.
[3] R. E. Melchers, npj Mater. Degrad. 2019, 3, 4.
[4] A. R. Marder, Prog. Mater. Sci. 2000, 45, 191.
[5] F. Chen, P. Liu, ACS Appl. Mater. Interfaces 2011, 3, 2694.
[6] Y. González-Garcia, S. González, R. M. Souto, Corros. Sci. 2007, 49, 3514.
[7] R. Cai, M. Sun, Z. Chen, R. Munoz, C. O’Neill, D. E. Beving, Y. Yan, Angew. Chem., Int. Ed. 2008, 47, 525.
[8] Q. H. Thi, H. Kim, J. Zhao, T. H. Ly, npj 2D Mater. Appl. 2018, 2, 34.
[9] C. Chen, S. Qiu, M. Cui, S. Qin, G. Yan, H. Zhao, L. Wang, Q. Xue, Carbon 2017, 114, 356.
[10] A. Krishnamurthy, V. Gadhamshetty, R. Mukherjee, B. Natarajan, O. Eksik, S. Ali Shojaee, D. A. Lucca, W. Ren, H.-M. Cheng, N. Koratkar, Sci. Rep. 2015, 5, 13858.
[11] S. Rigo, C. Cai, G. Gunkel-Grabole, L. Maurizi, X. Zhang, J. Xu, C. G. Palivan, Adv. Sci. 2018, 5, 1700892.
[12] A. Kumar, P. K. Vemula, P. M. Ajayan, G. John, Nat. Mater. 2008, 7, 236.
[13] a) G. Chilkoo, S. P. Karanam, S. Star, N. Shrestha, R. K. Sani, V. K. K. Upadhyayula, D. Ghoshal, N. A. Koratkar, M. Meyyappan, V. Gadhamshetty, ACS Nano 2018, 12, 2242; b) G. Chilkoo, N. Shrestha, A. Kutana, M. Tripathi, F. C. Robles Hernández, B. I. Yakobson, M. Meyyappan, A. B. Dalton, P. M. Ajayan, M. M. Rahman, V. Gadhamshetty, ACS nano 2020, 15, 447; c) G. Chilkoo, G. Jawaharraj, K. Vemuri, B. Vemuri, A. Kutana, M. Tripathi, D. Kota, T. Arif, T. Filleter, A. B. Dalton, B. I. Yakobson, M. Meyyappan, ACS nano 2020, 14, 14809.
[14] Y.-P. Hsieh, M. Hofmann, K.-W. Chang, J. G. Jhu, Y.-Y. Li, K. Y. Chen, C. C. Yang, W.-S. Chang, L.-C. Chen, ACS Nano 2014, 8, 443.
[15] D. Prasai, J. C. Tuberquia, R. R. Harl, G. K. Jennings, K. I. Bolotin, ACS Nano 2012, 6, 1102.
[16] W. Sun, L. Wang, T. Wu, M. Wang, Z. Yang, Y. Pan, G. Liu, Chem. Mater. 2015, 27, 2367.
[17] C. Cui, A. T. O. Lim, J. Huang, Nat. Nanotechnol. 2017, 12, 834.
[18] S.-M. Lee, J.-H. Kim, J.-H. Ahn, Mater. Today 2015, 18, 336.
[19] P. A. Tran, T. J. Webster, Nanotechnology 2013, 24, 155101.
[20] J. T. Weld, A. Gunther, J. Exp. Med. 1947, 85, 531.
[21] J. Xu, A. Asatekin, K. K. Cleason, Adv. Mater. 2012, 24, 3692.
[22] A. M. Diez-Pascual, M. A. Gómez-Fatou, F. Ania, A. Flores, Prog. Mater. Sci. 2015, 67, 1.
[23] S. Susarla, T. Tsafack, P. S. Owuor, A. B. Puthirath, J. A. Hachtel, G. Babu, A. Apte, B. I. Jawdat, M. S. Hilario, A. Lerma, H. A. Calderon, F. C. Robles Hernandez, D. W. Tam, T. Li, A. R. Lupini, J. C. Idrobo, J. Lou, B. Wei, P. Dai, C. S. Tiwary, P. M. Ajayan, Sci. Adv. 2019, 5, eaau9785.
[24] S. R. Bakshi, K. Balani, T. Laha, J. Tercero, A. Agarwal, JOM 2007, 59, 50.
[25] W. C. Oliver, G. M. Pharr, J. Mater. Res. 1992, 7, 1564.
[26] F. Cesano, D. Scarano, Graphene and Other 2D Layered Nanomaterial-Based Films – Synthesis, Properties and Applications, MDPI, Basel, Switzerland 2019.
[27] C.-Q. Ye, R.-G. Hu, S.-G. Dong, X.-J. Zhang, R.-Q. Hou, R.-G. Du, C.-J. Lin, J.-S. Pan, J. Electroanal. Chem. 2013, 688, 275.
[28] S. K. Burgess, R. M. Kriegel, W. J. Koros, J. Colloid Interface Sci. 1972, 45, 17.
[29] C. H. Hines, M. K. Tripodi, J. Membr. Sci. 2012, 3967.
[30] M. A. R. Saadi, B. Ulutu, C. H. Parvini, S. D. Solares, Surf. Topogr.: Metrol. Prop. 2020, 8, 045004.
[31] E. Sader, J. W. M. Chon, P. Mulvaney, Rev. Sci. Instrum. 1999, 70, 3967.
[32] C. P. Green, H. Liao, J. P. Cleveland, R. Proksch, P. Mulvaney, J. E. Sader, Rev. Sci. Instrum. 2004, 75, 1988.
[33] R. J. Cannara, M. Eglin, R. W. Carpick, Rev. Sci. Instrum. 2006, 77, 053701.
[34] M. D. Hanwell, D. E. Curtis, D. C. Lonie, T. Vandermeersch, E. Zurek, G. R. Hutchinson, J. Cheminf. 2012, 4, 17.
[35] M. J. Fisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G Scalmani, V. Barone, B. Mennucci, G. A. Petersson et al. Gaussian 09, revision A.1; Gaussian Inc.: Wallingford, CT, 2009.
[36] A. D. Becke, Phys. Rev. A 1988, 38, 3098.