Graphene-based anti-corrosive coating on steel for reinforced concrete infrastructure applications: Challenges and Potential

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Abstract

Steel corrosion has been a major perpetual issue of concern for durability and structural integrity of steel and reinforced concrete infrastructure. Polymeric, zinc-galvanic and chromate conversion coatings are commonly applied to protect typical steel materials such as structural steel, reinforcing steel bar (rebar), mild steel and light gauge steel used in infrastructure. Yet, due to physical integrity, long-term performance and environmental concerns, their applications have been limited. In recent years, graphene has garnered considerable attention in the field of anti-corrosive coatings and substantial progress has been achieved in the development of particular graphene-based monolithic (single/few-layer graphene and graphene oxides) as well as laminate and nanocomposite coatings. Despite considerable efforts dedicated towards fundamental research, the laboratory to industry transition of graphene-based anticorrosion coatings remains challenging. To this end, this report reviews the state-of-the-art on graphene-based coating technology with application to steel surfaces and discusses, both, experimental studies and theoretical aspects. Specifically, this review presents (i) production of different forms of graphene-based materials and the coating process; (ii) corrosion resistance and anti-corrosive coating performance of graphene-coated steel materials, (iii) key potential areas and challenges pertaining to the application of graphene-based coating to structural steel and rebar; and (iv) potential future directions towards corrosion protection and smart coatings.

Keywords: graphene, laminate, nanocomposite, coating steel, anti-corrosion.

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1. Introduction

Steel materials have wide applications in steel and reinforced concrete infrastructure development. Carbon steel (0.12-2.00% carbon) and alloy steel (carbon steel alloying other elements) grades commonly account for the production of structural steel, steel reinforcing rebar, mild steel, and light gauge steel. Structural steel with different shapes and hollow structural sections is extensively used as structural beams and columns in steel structure construction. Steel rebar typically made with carbon steel serves as a reinforcing agent in reinforced concrete structure construction. Over time, both the structural steel and rebar are susceptible to extensive corrosion when they are exposed to the corrosive environment such as in marine conditions or de-icing salt exposure. For example, corrosion of steel rebar can lead to the cracking of concrete, spalling, and staining of the reinforced concrete infrastructure, which is a major concern for the sustainability, safety, durability and economic implications pertaining to civil infrastructure [1]. In reality, corrosion of metals globally accounts for US$2.5 trillion annually [2], where a significant part of this cost is associated to the durability of steel and reinforced concrete structure. In the USA, the average direct cost of corrosion protection for highway concrete bridges in 2002 was estimated $8.3 billion annually which expected to be much higher in 2021 considering inflation [3].

Corrosion of steel rebar is a major durability concern in reinforced concrete materials systems. Steel rebar embedded in the concrete matrix are typically protected by a passive oxide layer developed in the interface due to a relatively high pH of concrete [4]. There are two common steel rebar corrosion mechanisms in concrete. One is the penetration of chloride ions through porous concrete such as in marine environment or sourced from de-icing salt which can cause pitting corrosion [5], and the other is the carbonation of concrete when atmospheric CO_2 reacts with portlandite of concrete at the presence of water and reduces the pH of concrete from approximately 13 to 9, which diminishes the protective passive layer of steel rebar [6]. Therefore, the effects of increasing chloride concentration to meet or exceed the critical chloride concentration and/or the reduction in pH value of the concrete pore solution, leads to the initiation of corrosion of steel rebar surface [7]. The corrosion of steel results in the loss of original cross-section, as well as up to six times the volume expansion causing debonding of rebar from concrete, ultimately resulting a failure of the composite material system and in turn affecting the integrity of the structure. Application of an anti-corrosive coating to structural steel and rebar embedded in concrete, can be an effective solution. Barrier protective coating systems, such as polymers (e.g., epoxy layer, paints), metal (e.g., iron-zinc alloy/ galvanizing), enamel (e.g., porcelain/vitreous made by fusing powdered glass) and nanoparticle-based composites (e.g., polyurethane-nano-SiO_2, epoxy with nano-SiO_2 or Fe_2O_3 or Zn, alkyd resin with nano-ZnO or nano-Al_2O_3) are typically used to restrict contact of moisture and oxygen to the surface of the steel [8–15]. However, these conventional coatings

have their respective limitations in performance and service life. Some common drawbacks include: chemical reactions in fresh concrete with galvanized bar, weak bond between steel and surrounding concrete with epoxy-coated bar, and brittleness of enamel coating [16]. These can result in abrasion of coating layer during transportation and construction handling, defects in the coating during fabrication, and lead to pitting corrosion. Polymer coatings are susceptible to high-temperature degradation and suffer from their inherent porosity. Furthermore, the use of thick coatings may disrupt the functionality (e.g. electrical and thermal conductivity) and component dimensionality of target metals [17,18]. Other approaches for carbon steel and alloy steel corrosion prevention are the use of cathodic and anodic protections, and stainless steel or glass fibre reinforced polymer (GFRP) as a costly alternatives have limitations in terms of bending, ductility, cutting and joining required for reinforced concrete infrastructure [19].

In comparison to traditional approaches, graphene has become a potentially important candidate for surface coatings against corrosion owing to its chemically inert nature and impermeability to gases and liquids, and is an emerging field of research [20]. As the strongest known material, graphene possesses an ultrahigh fracture strength (~100 GPa) [21], and ultrahigh fatigue life (>10^9 cycles) which can benefit a structure's integrity under severe and complex loading conditions [22]. Its superlubricity and ultralow friction further enables the graphene-based coating to exhibit desirable properties including, high wear and scratch resistance [23,24]. Moreover, other properties such as thermal conductivity (up to 5000 $Jm^{-1}K^{-1}s^{-1}$) and functionalization potential [25–29], are also crucial for retaining the functional properties of the metal beneath the coating. In addition, due to the atomic thickness (~0.34 nm), graphene considerably reduces the volume of coating material, compared to other more traditional coating materials. In light of the diversification of commercial barrier coatings that are application-specific, graphene can also be integrated with other barrier materials that complement each other (e.g. ceramic and polymer) to construct a laminate coating and a composite coating. In this scenario, graphene provides the barrier function, meanwhile ceramic and polymer offer other functionalities needed for an effective and long-lasting protection.

Despite substantial progress achieved in the fundamental research of graphene-based anti-corrosive coatings, the path from laboratory to industry poses daunting challenges. Some of the key significant challenges at stake for industrialization of graphene-based anti-corrosive coating include the quality control of graphene materials, scalable deposition of graphene-based coatings on substrates, long-lasting corrosion protection strategies, optimization of manufacturability to account for cost and reliability, and the corresponding environmental impacts. In contrast to review articles [30–36], that provided an overview of the scientific state-of-the-art and relevant technical details, in this review, we present a full account of challenges and potential of graphene-based coatings for anti-corrosion applications on structural steel and rebars, with a special emphasis towards their industrialization and commercialization. As outlined in Fig. 1, Section 2 will present three forms of graphene namely, monolithic, laminate, and nanocomposite coatings. For each type of graphene-based coating, the mechanisms which rely on the physics and chemistry behind the protective efficiency (e.g. impermeability, structural integrity, etc.), the preparation of coating materials and coating methods, anti-corrosion properties, common failure modes and mechanisms (e.g. defect, interface, etc.), and performance optimization measures are presented. Upon synthesis and critical review of the three coating options in terms of different factors (e.g. long-term stability, cost, scalability, quality and environmental sustainability), a recommended approach is presented for coating steel with application to infrastructure.

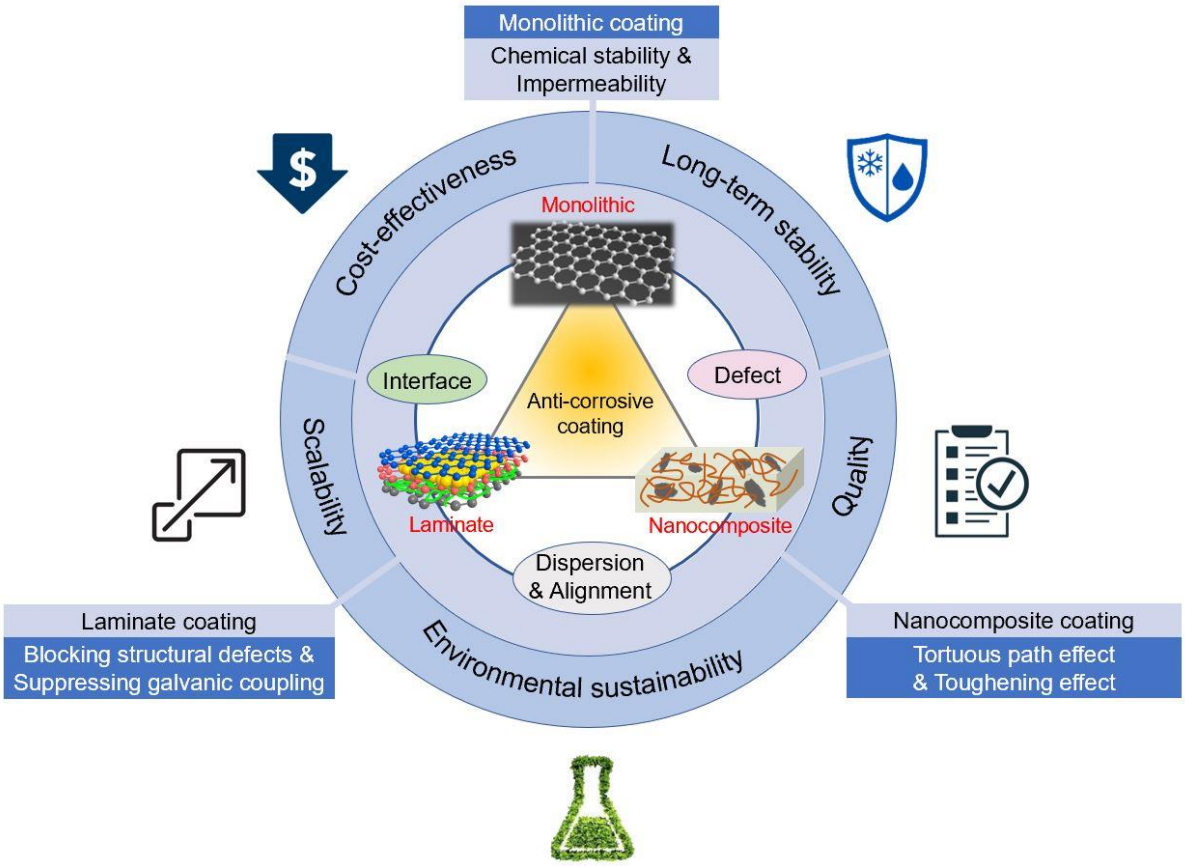

Fig. 1 Overview of graphene-based anti-corrosive coatings, including graphene-based monolithic, laminate and nanocomposite coating, showing coexistence of challenges and opportunities.

2. Graphene-based anti-corrosive coating

The development of graphene-based anti-corrosive coating for steel surfaces have progressed along three avenues: (i) graphene-based monolithic coating, (ii) graphene-based laminate coating, and (iii) graphene-based nanocomposite coating. For each coating category, the key advancements related to corrosion resistance and the corresponding synthesis and coating processes types based on literature reports are summarized in Table 1. In this section, a brief introduction of the three coating systems will be given, including corrosion protection mechanisms, preparation/coating methods and anti-corrosion performance.

Table 1. Materials processing and coating techniques and corrosion performances on the graphene-based anticorrosive coating on iron/steel surface.

Graphene-based monolithic coating						
Materials synthesis and coating process	Year	Coating thickness	Corrosion performance			Ref.
			Testing environment	Resistance	Rate	
CVD grown graphene on metals (Cu, Pt, Ni, Co, Fe) at low temperature (650 °C)	2015	Single layer graphene	Air exposure	Cu, Pt: weakly interacting, ready access for oxidizing Ni, Co: Strongly interacting, passivating oxide Fe: Strongly passivating, non-passivating oxide so initially slow but accelerate in long term exposure	No data reported	[37]
CVD grown graphene on Ni-buffered SS at 700-900 °C (Ni/SUS304)	2015	Single to multilayer graphene	3.5 wt% NaCl solution	ICR increases after 20 scans in Graphene, Ni/SUS304: 30 → 36 mΩ cm^2 SUS304: 158 → 560 mΩ cm^2	Corrosion resistance, $I_{current}$ ($A\text{-}cm^{-2}$) after 20 scans in: SUS304: $1.49\times10^{-7} \rightarrow 7.41\times10^{-6}$ Graphene-Ni/SUS304: $1.61\times10^{-7} \rightarrow 1.63\times10^{-7}$ (~45 times lower than SUS304);	[38]
CVD grown graphene on SS at low temperature (400°C)	2016	Single or few-layer graphene	5% wt.% sea salt solution	Stable and long-lasting anticorrosion after long-term immersion	Corrosion rate lowers up to 10 times, Bare steel: 1.75×10^{-13} $m.s^{-1}$ Coated steel: 2.02×10^{-14} $m.s^{-1}$ (~9 times lower than bare steel)	[39]
Graphene grown on carbon steel by laser processing	2015	Multilayer graphene	3.5% wt.% NaCl aqueous solution	Up to ~1900 Ω cm^2, almost 7 times that of original steel (270.7 Ω cm^2).	0.05 mm/year, much lesser than that of the stainless steel (0.09 mm/year)	[40]
rGO ink coated Fe sample	2013	1.2–1.4 nm	1% wt.% NaCl solution	Coating resistance increases from 17 Ωcm^2 for bare Fe to 766 Ω cm^2 for graphene ink/Fe	No data reported	[41]
rGO nanosheets deposited on carbon steel by	2016	/	3.5% NaCl aqueous solution	Corrosion current density (J_{corr}): 69.2 μA cm^{-2} for bare carbon steel	0.804 mm/year for bare carbon steel surface → 0.354 mm/year for rGO coated carbon steel	[42]

electrochemical deposition				surface → 30.5 μA cm^{-2} for rGO coated carbon steel		
Electrophoretic deposition of GO onto carbon steel	2017	Less than 10 nm	3.5% wt.% NaCl aqueous solution	Corrosion current density: 11.83 ± 0.86 mA cm^{-2} for uncoated carbon steel → 4.14 ± 0.64 mA cm^{-2} for GO coated carbon steel	Reduce up to three times the corrosion rate of carbon steel	[43]
GO drop casting onto carbon steel rebar	2021	Several layer of GO	Concrete pore solution with 3.0 % wt.% NaCl	GO coating increases the resistance to 4150.47 Ω cm^2 from 294.47 Ω cm^2 for uncoated steel	Corrosion rate decreases in GO coated steel to 0.0089 mm/year from 0.85 mm/year in uncoated	[44]
Graphene-based laminate coating						
Materials synthesis and coating process	Year	Coating thickness	Corrosion performance			Ref.
			Testing environment	Resistance	Rate	
Al_2O_3/TiO_2/rGO by ALD on SS	2016	⩽200 nm	3.5% wt.% NaCl aqueous solution	3.8 × 10^6 Ω cm^2 for bare SS → 4×10^7 Ω cm^2 for SS/rGO/ceramic laminate	No data reported	[45] [46]
CVD graphene/PVB hybrid films by spin coating-assisted layer-by-layer assembly on AA	2014	4–5 μm	APS copper etchant	Corrosion current density: 4×10^{-5}–4×10^{-7} A cm^{-2} for bare AA → 10^{-10} A cm^{-2} for CVD graphene/PVB laminate coated AA	4 μm/year for bare AA → <2 nm/year for AA/CVD graphene/PVB laminate	[47]
hBN/MoS_2/PVA drop cast on SS	2013	5 μm	3.5% wt.% of API salt aqueous solution	Corrosion current density: 6.46×10^{-6} A cm^{-2} for MoS_2 coated SS → 4.50×10^{-6} A cm^{-2} for hBN/MoS_2 laminate coated SS	No data reported	[48]
	Graphene-based nanocomposite coating					
Materials synthesis and coating process	Year	Coating thickness	Corrosion performance			Ref.
			Testing environment	Resistance	Rate	
0.1-0.3 wt% GO in WPU dispersion, solution blending (PVA, Zinc oxide, CB) and dipping of MS	2015	15–20 μm	3.5% wt.% NaCl solution	Corrosion resistance: Rct–0.3% PGZ and PCZ = 34.21 and 27.08 kΩ cm^2 Overall PVA anchored GO/ZnO > CB/ZnO	0.3% PGZ and PCZ = 56.85 and 10.37 kΩ cm^2 Corrosion rate of MS/WPU/0.3% PGZ and PCZ are almost 147 and 31 times lower than bare MS	[19]

Graphene (high shear mixing + bath sonication), functionalized with APTES in water and applied by a bar applicator	2015	4 µm, Dry film (30±5 µm)	3.5% wt.% NaCl solution (pH 5.5 at 25 °C)	Corrosion resistance (R_{ct}+R_f): Mild Steel = 550 kΩ cm^2, Chromate pre-treatment+Primer =1.6×10^6 kΩ cm^2; Graphite+Primer = 2.4×10^5 kΩ cm^2; Functionalized graphene +Primer = 2.8×10^6 kΩ cm^2	Corrosion rate (mils penetration per year): Mild Steel = 30.386, Chromate pre-treatment+Primer = 0.087; Graphite+Primer = 1.732; Functionalized graphene +Primer = 0.015 (~2026 times lower than MS),	[49]
Composite mixed (wt%): APTES: 39.96-38; Water: 59.94-57; Graphene: 0.1-5. Coating was applied on MS by bar applicator and heat treated at 200 °C	2017	3-µm dry film; 20 µm (wet film thickness)	3.5 wt.% NaCl solution (freely exposed to air, pH 5.5 at 25 °C)	The amount of water absorbed at saturation decreases with increasing graphene concentration up to 5% loading (74% reduction at 288 hours exposure) compared to APTES coated MS	EIS measurement in coated MS surface: APTES coating: 288 h severely damaged 5% graphene composite coating: far less damage even after 480 h of exposure.	[50]
GO, amino-terminated IL, epoxy composite using a grafting reaction (Q235) coated by a bar coater on Steel	2018	30 ± 2 µm	3.5 wt.% NaCl aqueous solution	Salt spray test on steel: Pure epoxy and the epoxy 0.5 wt% rGO coating showed corrosion after 100 h, IL-GO composite coating was relatively clean after 300 h	Corrosion current changes: Epoxy-coated: 3.10 (1h) → 4.75 µA·cm^{-2} (30h) IL-GO-coated: 2.20 µA·cm^{-2} (30 h)	[51]
GO synthesised heating *Aeschynomene aspera* plant at 1600 °C in an argon atmosphere; Cup-milling GO and sunflower oil (10 min), dip-coating on CR steel, and curing at 350 °C for 10 min at atmosphere	2015	0.8 µm	3.5 wt.% NaCl aqueous solution	Salt spray test: Red rusting in RC steel, GO ink coated: 100 h Oil coated: 24 h Bare (no coating): 6 h	Corrosion rate (mm/year) in CR steel: GO ink coated: 0.0000075 (10,000 times lower than bare steel) Oil coated: 0.01159 Bare (no coating): 0.1069	[52]
rGO from secretion products of insect, *Laccifer Lacca* then PT: rGO dip coating heated at 710 °C for 24 h, and dip	2018		3.5 wt% NaCl aqueous solution at pH 7.3 and at room temperature (20 ± 2 °C)	EIS coating polarisation resistance, R_p: Bare: 0.99 kΩ cm^2 rGO coated: 0.62 kΩ cm^2 SO coated: 1.78 kΩ cm^2	Corrosion rate (mm/year) in CR steel: Bare: 0.17958 rGO coated: 0.18922 SO coated: 0.03994	[53]

coated CR steel in sunflower oil at 350 °C for 10 min				PT coated: 823.2 kΩ cm^2	PT coated: 0.000017 (10,000 times lower than bare steel)	
Exfoliation and functionalization of graphite with ABA in PPA/P_2O_5 then polyaniline/graphene 0.5 wt.%) composites (PAGCs) grafted on steel	2012	29 µm	3.5 wt.% NaCl aqueous solution	EIS, polarisation resistance, R_p: Bare: 2.48 kΩ cm^2 PAGCs coated: 135.22 kΩ cm^2 Protection efficiency ($P_{Tahmina}$ %): Bare: None PAGCs coated: 53.49 PAGCs reduces water permeability 10 times than bare steel	Corrosion rate (mm/year) in CR steel: Bare: 0.1722 PAGCs coated: 0.0044 (39 times lower than bare steel)	[54]
Hydrophobic epoxy graphene composite (HEGC) mixed using three-roll mill and CR steel coated using a nanocasting technique	2014	Epoxy: 110 µm HE: 110 µm HEGC: 115 µm	3.5 wt.% NaCl aqueous solution	EIS, polarisation resistance, R_p: Bare: 2.94 kΩ cm^2 Epoxy: 25.46 kΩ cm^2 HE: 37.87 kΩ cm^2 HEGC: 442.00 kΩ cm^2	Corrosion rate (mm/year) in CR steel: Bare: 0.1648 Epoxy: 0.0254 HE: 0.0089 HEGC: 0.0023 (72, 11 and 4 times lower than bare, Epoxy and HE coating, respectively)	[55]
Poly (EVOH)-BA-GO compounds mixed using stirring and ultrasonication then spray coated on SS	2018	21± 1 µm	3.5 wt.% NaCl aqueous solution	EIS, polarisation resistance: Bare SS: 11 kΩ cm^2 EVOH: 300 kΩ cm^2 EVOH-BA-GO: 610 kΩ cm^2	Corrosion rate (mm/year): Bare SS: 0.2540 EVOH: 0.0247 EVOH-BA-GO: 0.0034 (~75 times lower than bare SS)	[56]
GO, rGO,MWCNT mixed to two-part epoxy resin painted with brush	2022	270 ± 40 µm	Concrete from OPC	EIS corrosion current (90 days): Bare: 0.22A (29d); PE: 0.1 A rGO/CNT: 0.04A; GO/CNT: No	Mass loss in rebar: Bare: 24.5%; PE: 11.3% rGO/CNT: 8.6%; GO/CNT: 0.45%	[57]

Note: AA: Aluminium alloy; ABA: 4-aminobenzoyl acid group; APTES: 3-(Aminopropyl) triethoxysilane; BA: Boric acid; CB: Carbon black; CR: cold-rolled; CS: Carbon steel; CVD: Chemical vapor deposition; EIS: Electrochemical impedance spectroscopy; EVOH: Poly(vinyl alcohol-co-ethylene); GO: Graphene oxide; ICR: Interfacial contact resistance; IL: Ionic liquid; MS: Mild steel; PPA: Polyphosphoric acid; PVA: Polyvinyl alcohol; PVB: polyvinyl butyral; SS: Stainless steel; SST: Salt spray test; WPU: Waterborne polymer.

2.1. Graphene-based monolithic coating

2.1.1. Corrosion protection mechanism

Albeit being only one-atom thick, pure defect-free graphene can be completely impermeable to gases (neon, nitrogen, oxygen, argon, krypton and xenon) and liquids, thus inducing the barrier effect to protect the coated metal or steel surface from corrosion reactions [58]. This impermeability is mainly due to the hexagonal lattice structure of graphene, where a geometric pore size of diameter 0.064 nm is formed (Fig. 2a), which is even smaller than the helium atom [58]. The impermeability has been demonstrated through a graphene-sealed microchamber. The deflation in air was captured by slowly decreasing bubble deflection, as shown in Fig. 2b. The leak rate was estimated by monitoring the pressure change which reached 10^5–10^6 atoms/s for helium (Fig. 2c) [59]. More recently, Sun *et al.* fabricated a new type of microwells with impermeable monocrystalline walls (Fig. 2d and 2e), and found the leakage rate to be as low as 10^{-4} atoms/s, enabling the permeation of just a few helium atoms per hour (Fig. 2f) [60]. In addition, the high chemical stability of graphene further improves the oxidation resistance of coatings and leads to passivation of the metal underneath in the active oxidation environments [61].

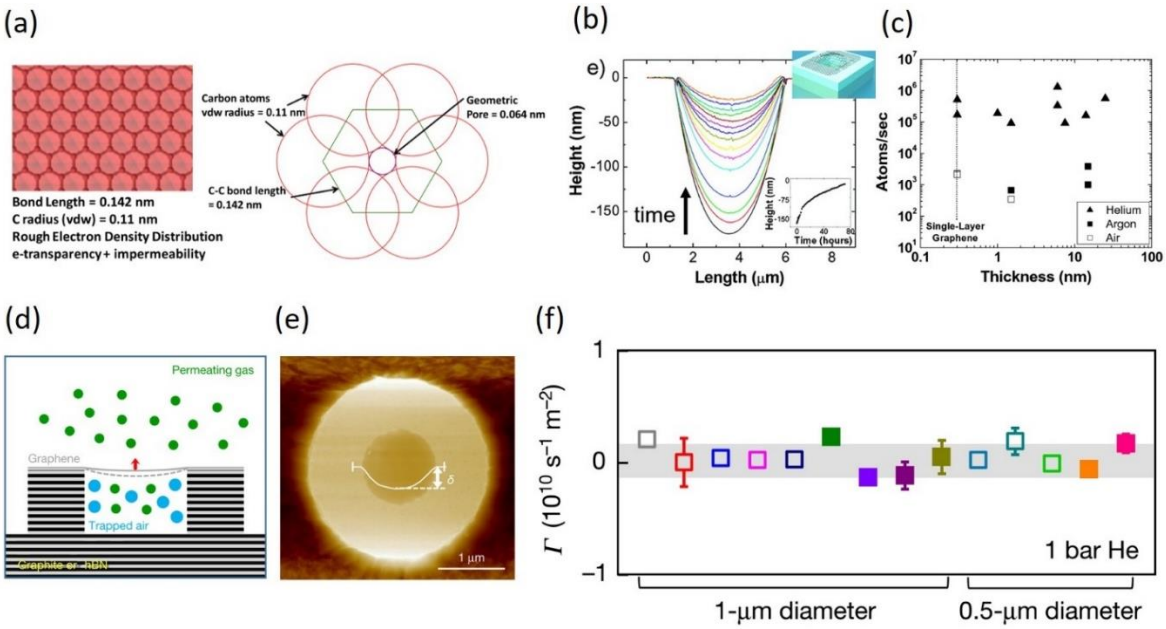

Fig. 2 (a) Atomic structure of monolayer graphene with rough electronic density distribution. Reproduced with permission from Ref. [58]. Copyright 2013, Elsevier. (b) The AFM line profile of inward bubble deflection showing the air leakage over time. (c) Leakage rate as a function of graphene thickness for different gases. Reproduced with permission from Ref. [59]. Copyright 2015, American Chemical Society. (d) Schematic and (e) AFM image of graphene-sealed monocrystalline microchamber. (f) Leakage rate evaluated based on 14 samples placed in helium over a one-month period. Reproduced with permission from Ref. [60]. Copyright 2020, Springer Nature.

2.1.2. Preparation/coating methods

The most straightforward way to cover a metal substrate with a graphene-based monolithic (single or few layer) coating is to simply synthesize graphene film directly on to its surface. Chemical vapour deposition (CVD) is a commonly used method (Table 1) for the large-area synthesis of graphene films (Fig. 3a). It not only allows a direct, facile, large-scale and transfer-free graphene coating process, but also affords graphene production with good quality, coverage uniformity and a clean interface with the underlying metal materials [62,63]. A direct growth of graphene on different types of steel can be achieved using low-temperature methods [63].

Mass production of graphene for anti-corrosive coating can also be realized by liquid exfoliation. In particular, graphene nanoplatelet (GNP) can be separated from graphite in aqueous solutions through sonication, accompanied with an oxidation-reduction process [64]. The key issue here is the presence of excessive structural defects within the graphene lattice. In contrast, liquid phase exfoliation has been demonstrated to offer a scalable and cost-effective route to produce high-quality, unoxidized graphene from powdered graphite [65]. The high-shear liquid exfoliation is able to achieve the exfoliation in liquid volumes from hundreds of millilitres up to hundreds of litres and beyond (Fig. 3b) [66]. These dispersions can then be used to deposit flakes by dip coating, spray coating and other coating methods.

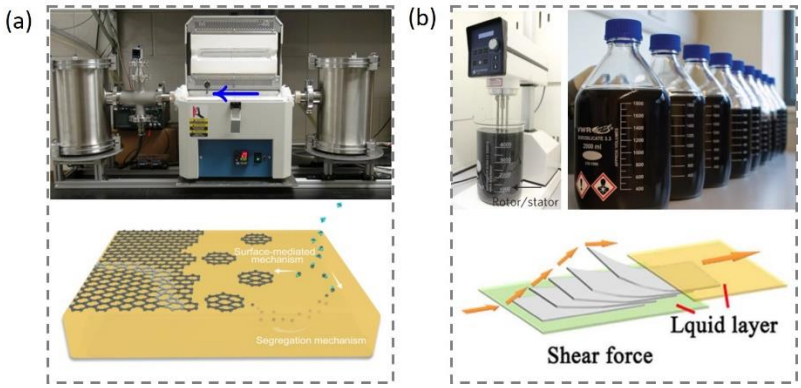

Fig. 3 (a) Chemical vapour deposition system configured for graphene growth on metallic substrate. Reproduced with permission from Ref. [62]. Copyright 2018, American Chemical Society. Reproduced with permission from Ref. [67]. Copyright 2015, Springer Nature. (b) Scalable production of few-layer graphene with high-shear liquid exfoliation method. Reproduced with permission from Ref. [66]. Copyright 2014, Springer Nature. Reproduced with permission from Ref. [68]. Copyright 2014, The Royal Society of Chemistry.

2.1.3. Anti-corrosion performance

CVD grown graphene coating has been demonstrated to protect the surface of steel from corrosion as evidenced in the literature summarized in Table 1. Facing the challenge to synthesize graphene directly on steels, Zhu *et al*. proposed a generalizable low-temperature (~300°C) CVD method to fabricate large-area and low-defect graphene-based monolithic coatings with single to few layers [39]. Electrochemical corrosion results showed that the corrosion rate of graphene-coated stainless steel was reduced by 9 times compared to bare steel (i.e., non-coated steel) without graphene protection, as shown in Fig. 4. Even immersed in a sea salt solution (5%) for 30 days, the corrosion rate maintained relatively low with graphene coating, which indicated an effective anti-corrosion performance in harsh environment [39]. To facilitate the graphene growth on carbon steel, Ye *et al*. adopted a laser induction technique to introduce nickel element into carbon steel and overcame the CVD temperature limitation [40]. Electrochemical impedance spectroscopy (EIS) was carried out following 1 h immersion of samples in 3.5% NaCl aqueous solution. The results indicated that the corrosion rate for graphene-coated carbon steel was much less compared to that of bare stainless steel. The corrosion resistance could reach a high level, almost 7 times that of bare carbon steel and comparable to that of bare stainless steel [40]. More quantitative descriptions are detailed in Table 1.

While graphene oxide (GO) films fail to provide effective shielding against gases and liquids mainly due to the loose stacking and defective structures [69], the chemical or thermal reduction aids to reduce the interlayer separation and restores the graphene lattice by removing oxygen functional groups [70]. It is therefore, reasonable to expect an improvement in corrosion resistance for reduced GO (rGO) coatings, since the properties of rGO is somewhat comparable to pristine graphene. Mayavan *et al*. indicated that the rGO monolithic coating is more capacitive than resistive, hence, providing protection

against corrosion of iron [41]. Bagherzadeh *et al*. coated rGO nanosheets on carbon steel and realized a 67.2% increase in protective efficiency on rGO-coated carbon steel compared to their bare counterpart [42]. A reduction up to three times in the corrosion rate was observed, accompanied with an increase in charge transfer resistance and a decrease in corrosion current (Table 1) [43]. The high degree of oxidation resistance of the rGO film is exemplified in Fig. 4e, where the colour of the bare iron changed to brown after oxidation while the rGO-coated iron remained almost unchanged [71].

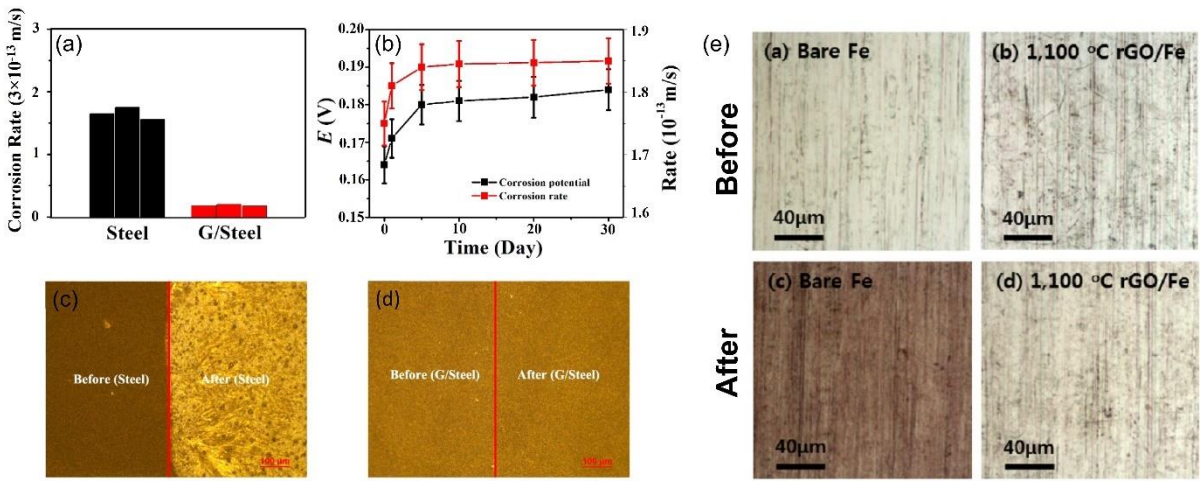

Fig. 4 (a) Corrosion rates of stainless steel and graphene/stainless steel (G/steel) samples. (b) Corrosion potentials and corrosion rate as a function of the time in the G/steel sample. Optical images of (c) pure stainless steel and (d) G/steel substrate before and after electrochemical anticorrosion testing. Reproduced with permission from Ref. [39]. Copyright 2016, American Chemical Society. (e) Optical images of bare and rGO-coated iron foils before and after oxidation at 200 ℃ in air for 2 h. Reproduced with permission from Ref. [71]. Copyright 2012, American Chemical Society.

Durability performance of steel rebar within concrete is a vital factor in civil infrastructure. Corrosion performance of a carbon steel rebar coated with GO (drop casting several times along with electron reduction) was investigated in a simulated concrete pore solution with 3 wt.% NaCl [44]. This was to provide an understanding of the durability performance of GO coated steel rebar embedded in a concrete matrix. GO coating reduced the corrosion current by almost three times to that of uncoated steel rebar. This resulted in a nearly 95 times reduction in corrosion rates of GO coated steel rebar (0.85 mm/yr) compared to uncoated steel rebar (0.85 mm/yr).

2.2. Graphene-based laminate coating

2.2.1. Corrosion protection mechanism

Graphene-based laminate coating, featuring multi-layered heterogeneous structures with alternating materials (e.g. polymer, ceramic, etc.), is proposed to build a thicker barrier on the metal surface. Typically, ceramics or polymers are deposited on graphene-based monolithic coatings as protective layers. For example, the alumina films with only a few atoms in thickness have exhibited outstanding impermeability to standard gases (e.g. oxygen), thanks to their pinhole-free structures [72]. These protective layers can not only passivate the defects in graphene but also minimize the external effects, such as mechanical scratches or local heating. Coatings can be subjected to complex stresses during practical use scenarios. Depositing several thin layers which have different mechanical properties can help to reduce the stress concentration and change crack propagation conditions [73]. The multi-layered

structure can be more compact and ordered for graphene coating composed of nanoplatelets, with the potential to markedly suppress cohesive failure. In addition to the structural protection and the passivation of defects, the introduced protective layers are insulating and therefore, also serve to break the galvanic coupling between graphene and metal substrate. In this respect, the insulating nature of hexagonal boron nitride (hBN) can reduce galvanic corrosion [74]. Moreover, hBN has the same hexagonal structure as graphene and therefore also possesses similar impermeability and mechanical strength [75,76], which makes the vertically stacked graphene/hBN heterostructure coating more promising in corrosion prevention applications than pure graphene-based monolithic coating, especially for the requirement of nanoscale thickness for anti-corrosive coatings.

2.2.2. Preparation/coating methods

Among thin film fabrication techniques, atomic layer deposition (ALD) has demonstrated potential advantages in producing dense and uniform ultrathin films/coatings [77–79]. The ALD process involves self-limiting surface reactions from the gas phase with atomic monolayer precision. This permits perfect conformal coatings for thin films, even on surfaces with complex shapes [80]. More importantly, as the C–C bonds in heptagon-pentagons present in the grain boundaries in graphene are highly strained and reactive, the ALD allows the selective deposition of metal or metal oxide on graphene's grain boundaries and cracks due to the enhanced chemical reactivity (Fig. 5a) [81,82]. By controlling the deposition parameter, ALD layer thickness can be increased to achieve the complete sealing of surfaces, which would benefit the anti-corrosion performance of the laminate coatings.

The laminate coating can also be fabricated through an alternative stacking of graphene and polymer layers (Fig. 5b). In particular, layer-by-layer assembly is well acknowledged as an efficient route for manufacturing highly ordered multilayer film structures. The advantages of this technique include the versatility of substrate options, the nanoscale control over the film thickness, the precise tailoring of graphene-polymer interface and the fine tuning of the surface morphology [83,84]. By far several deposition methods have been demonstrated for the layer-by-layer processing, such as dip coating, spin coating, spray coating, vacuum filtration, Langmuir-Blodgett deposition and so forth [85].

Regarding the graphene/hBN hybrid coating, in situ CVD growth method with practical scalability, high uniformity and quality has been documented [86]. However, the most versatile technique for the construction of heterostructure is direct mechanical assembly (Fig. 5c) [87]. Recently, state-of-the-art transfer methodologies have been comprehensively reviewed, such as polydimethylsiloxane (PDMS) exfoliation, vdW pick-up and PMMA (polymethyl methacrylate) carrying layer method [88,89].

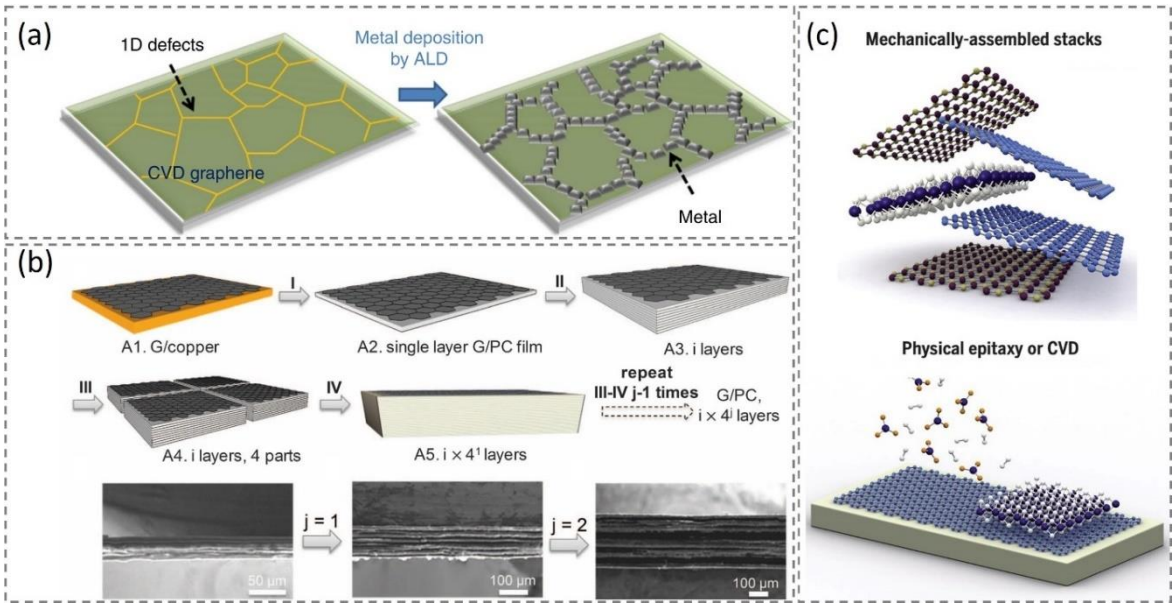

Fig. 5 (a) Selective platinum growth by ALD on one-dimensional defect sites of polycrystalline CVD graphene. Reproduced with permission from Ref. [81]. Copyright 2014, Springer Nature. (b) Fabrication of graphene/polycarbonate layers with aligned CVD, comprising spin coating, etching and stacking procedures. Reproduced with permission from Ref. [90]. Copyright 2016, The American Association for the Advancement of Science. (c) Production of van der Waals heterostructures, including mechanically assembled stacks and large-scale growth by CVD or physical epitaxy. Reproduced with permission from Ref. [87]. Copyright 2016, The American Association for the Advancement of Science.

2.2.3. Anti-corrosion performance

Improved anti-corrosion performance has been reported for CVD grown graphene coating covered with ALD alumina layer (Table 1). By tuning the size of ALD-generated particles and ALD cycles, the openings in the graphene coating could be selectively passivated, as evidenced by AFM images showing the change in morphology (Fig. 6a). As the ALD film thickness increases, a decrease in etch pit density can be observed. The continuous film is formed after 160 ALD cycles (Fig. 6b), which correspondingly leads to an inhibition efficiency of >99% (Fig. 6c) [47]. Mondal *et al*. further deposited alternating layers of alumina (Al_2O_3) and titanium dioxide (TiO_2) on rGO films by ALD technique and studied the anti-corrosion performance of such laminate coatings on stainless steels [45]. While the individual layer coating (rGO or Al_2O_3/TiO_2) failed to provide the corrosion protection alone, the combined laminate coating proved to be stable and resistive against pitting (Fig. 6d). The increased impedance of the interface and the pitting potential (Table 1) could be attributed to barrier effect of the film and shielding of the local electrical fields [45].

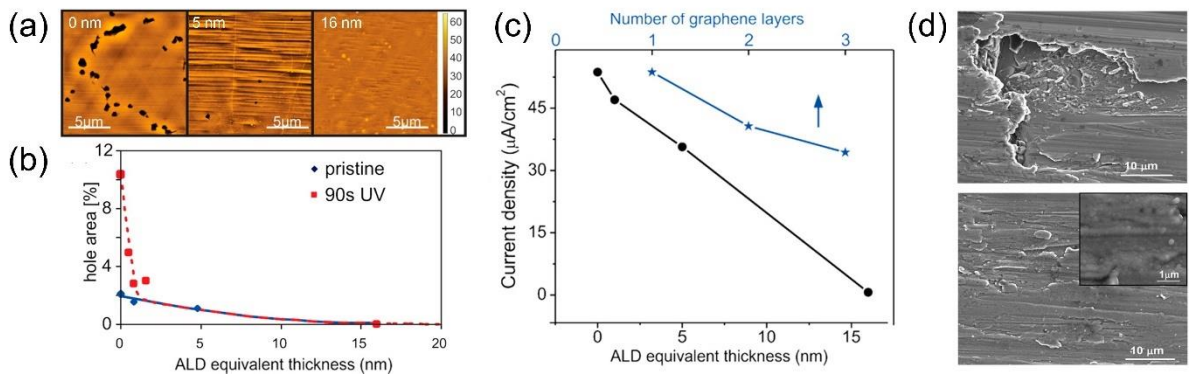

Fig. 6 (a) AFM topography image of etched graphene with ALD film of different thicknesses. (b) Copper hole area after deposition of ALD films on graphene coating. (c) corrosion current density as a function of ALD film thickness. Reproduced with permission from Ref. [47]. Copyright 2014, American Chemical Society. (d) SEM images of Al_2O_3/TiO_2 coating with and without rGO on stainless steel after 30 days of immersion in neutral pH, 3.5 mass% NaCl aqueous solution. Reproduced with permission from Ref. [45]. Copyright 2016, Elsevier.

Polymeric materials have also been widely used in layer-by-layer assembly with graphene for the anti-corrosion applications. Yu *et al*. prepared a series of CVD graphene/polymer laminate coatings through a spin coating-assisted assembly process (Fig. 7a) [91]. By conducting electrochemical tests, it was found that the pure polymer coating failed in protecting the metal after less than 30 days, while the laminate coating exhibited a higher corrosion resistance (Fig. 7b and Table 1). The corrosion protection mechanism rests on the construction of the laminate structure, which exploits the impermeability of graphene as well as the adhesive and insulating properties of the polymer layers [91]. Researchers have also reported the corrosion prevention applications of hBN films in marine coatings applied on stainless steel [48]. Recently, the effect of stacked MoS_2/hBN vdW heterostructure coating on the corrosion behaviour of steel (SS304) has been investigated. By comparison, the incorporation of hBN in between MoS_2 layers was found to improve its corrosion resistance as hBN layers constrained the charge carrier mobility [92]. Thus, it can be envisioned that graphene coating would also benefit from having hBN layers intercalated so that the galvanic coupling could be blocked to prolong the lifetime of coating.

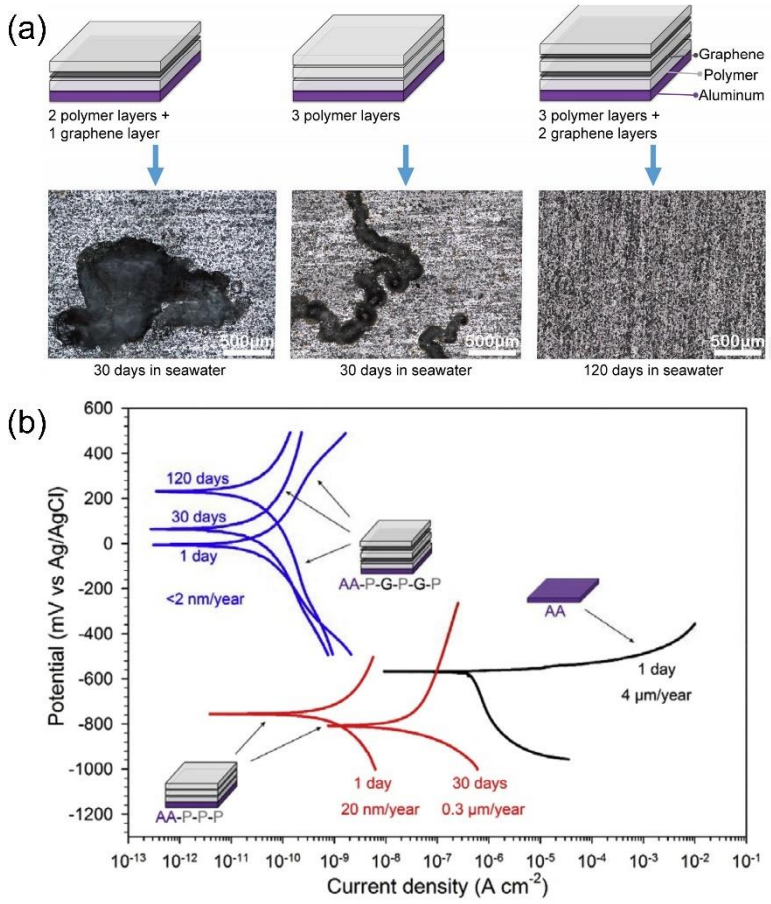

Fig. 7 (a) Corrosion morphology and (b) Potentiodynamic scans for bare polymer and polymer/graphene laminate coatings after long-lasting immersion in 3.5 wt% NaCl solution. Reproduced with permission from Ref. [91]. Copyright 2018, Elsevier.

2.3. Graphene-based nanocomposite coating

2.3.1. Corrosion protection mechanism

Adding graphene and its derivatives as fillers into conventional organic coatings represents another protection strategy pertaining to the corrosion of metals. This approach mainly takes advantage of the chemical inertness and corrosion resistance of graphene to extend the propagation path length of the corrosion medium in the coatings. As shown in Fig. 8a, the diffusion pathway of corrosive molecules such as H_2O, Cl^- is considerably twisted and prolonged by the graphene materials is termed as tortuous path effect. Such a barrier mechanism endows polymer/graphene nanocomposite with a higher potential in advanced anti-corrosive coating material compared with traditional polymer/clay composites [54].

Additionally, graphene aids to effectively prevent or retard cracking by strengthening and toughening the polymer film coating. This is possible by way of the following mechanisms: (i) graphene fillers can efficiently bear the load through the stress transfer across interfaces so as to improve the fracture resistance of the coating [93–95]; and (ii) once cracks are initiated and propagated into polymer matrix, they can be deflected/blunted by graphene to increase the crack pathway required to fracture the material [96,97]. Meanwhile, the weak interactions between graphene and the polymer matrix facilitate the interfacial sliding and result in graphene pull-out and crack bridging (Fig. 8b) [98,99]. These phenomena all induce more energy dissipation and account for the toughening mechanism. The consequent delay of crack propagation increases the duration and service life of graphene nanocomposite coatings.

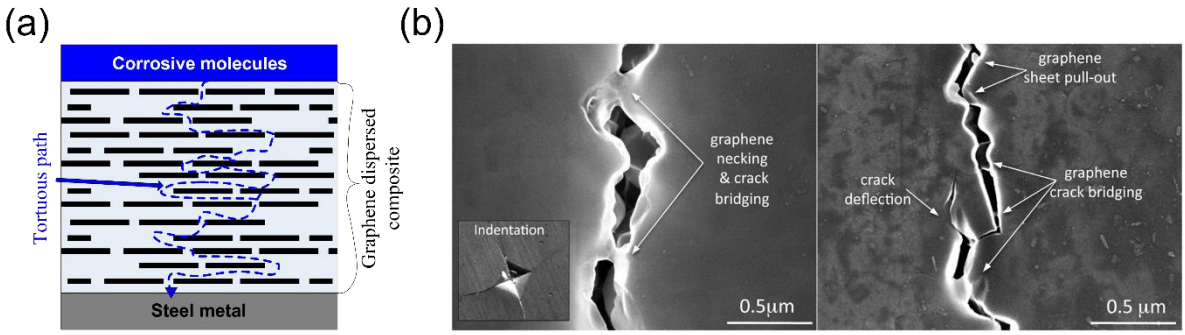

Fig. 8 (a) Schematic of tortuous path effect. (b) Typical fracture toughening mechanisms in graphene-based nanocomposite. Reproduced with permission from Ref. [96]. Copyright 2011, American Chemical Society.

2.3.2. Preparation/coating methods

The graphene-based nanocomposite coatings are commonly prepared with polymer-based GNP or GO dispersed compounds. Depending on the graphene filler types, different techniques and coating processes have been adopted for improved coating and anti-corrosion performance (Table 1). Typically, GNP/polymer-based nanocomposite coatings are produced through dispersing GNP in epoxy with solvents and acids using either or combination of magnetic stirring, roll mill and ultrasonication techniques at different temperature and mixing sequencing, then casting of GNP-polymer solution on steel substrates. GO/polymer-based nanocomposite coatings, on the other hand, are produced either by direct mixing of GO in polymer, or most popularly water/solvent borne GO in polymer-based composite; subsequently, drop casting, bar coater and spray gun can be used for coating over steel substrate. However, it should be noted that, direct mixing of GO without the aid of any solvent or water is found not to be a promising approach for coating steel metal surface. The is due to the fact that

effective dispersion of GO nanofillers in the polymer base media is the key issue to produce desirable polymer nanocomposite coating, and wet transfer method with rigorous mixing is typically used to achieve this desirable state. The surface functionalization of GO is crucial to the interface design and performance control of GO/polymer nanocomposite coating [100]. Typically, amino polymers, silanes, amines, ionic liquids and nanoparticles are used for the functionalization of GO, which encourage reactions between amine and epoxy, amine and carboxyl or salinisation for improved coating performance [101]. The functionalization of GO improves the interaction between GO and epoxy resins, as well as reduces the aggregation potential of GO sheets. In addition, the solvents used for preparation of solvent borne epoxy/GO nanocomposite coating are typically low-polar solvents used in painting applications [101]. Experiments have shown that GO is hydrophilic in nature [102]. When studying the effect of organic solvents, different interactions become relevant, for example, dispersion interactions, donor-acceptor, and electrostatic interactions in the presence of ions. Furthermore, the desired outcome also depends on the polarity of the solvent used [103].

2.3.3. Anti-corrosion performance

Effective composition of 2D graphene with the base materials eliminates the limitations of coating bonding with steel substrate and impacts of graphene defects on the corrosion mechanisms, thus yielding superior anti-corrosion performance on steel compared to that of graphene-based monolithic coating and laminate coating, as indicated in Table 1. For instance, roller coating and subsequent imidization of the nanocomposite blends yielded well-adhered GNP/polyetherimide (PEI) coating on steels. Potentiodynamic testing and sea salt water immersion tests indicated more than three orders of enhancement in efficacy of corrosion protection as compared with bare low-alloy steel. The inclusion of graphene also reduces corrosion by an order of magnitude over the pure polymeric coating [104]. Upon application of highly crystalline graphene integrated polyaniline nanostructured composites as corrosion protection coatings, Mahato *et al*. reported a decline in corrosion current up to ~3–4 orders of magnitude for coated mild steel surface in 0.1 M HCl [105]. Similar anti-corrosion performance was also observed for a hydrophobic epoxy/graphene nanocomposite coating on cold-rolled steel surface as detailed in Table 1 [55].

GO/polymer-based nanocomposite coating shows considerable efficiency in the anti-corrosion performance as well. Liu *et al*. studied the anti-corrosion performance of imidazole ion grafted GO composite [51]. The salt spray test results indicate that pure epoxy and rGO/epoxy coated steel substrates corrode at the scratch after immersing in NaCl solution for 100 h, while imidazole ion grafted GO/epoxy-based hybrid composite coating protects the steel surface from corrosion even after 300 h (Fig. 9b). Furthermore, the hybrid composite coated steel shows the minimal corrosion current and highest interfacial adhesion compared with other two systems (Fig. 9a). These observations indicated that the imidazole ion grafted GO/epoxy hybrid coating effectively enhanced the anti-corrosion performance of steel as well as prevented the detachment of coating from the steel surface. Singhbabu *et al*. studied an oil-based GO ink for anti-corrosive coating of cold-rolled steel [52]. The evaluation of the corrosion properties in the cold-rolled steel substrates from the open circuit potential measurements shows that the potential moves towards the positive potential by the coating of oil and a greater shift is observed in GO ink-coated steel substrate (Fig. 9c). The corrosion rate of bare cold-rolled steel is found to decrease by over 10,000 times with assistance of the GO-ink coating (Table 1). Another study similarly reported that a rGO sunflower-based ink coating suppressed the corrosion rate of cold-rolled steel by nearly 10,000 times compared to bare cold-rolled steel [53]. The red rusting in the cold-rolled steel due to the salt spray test initiated in GO-ink coated cold-rolled steel after 100 h in contrast to that of 24 h and 6 h for the oil-coated and bare steel, respectively (Fig. 9d). Overall, the oxygen functional groups of oil may result a chemical bonding with the metal and GO which produce an impermeable

coating layer with good adhesion on the steel surface. In fact, these values are higher than the reported corrosion rate of composite coatings containing polyaniline/graphene (10 times) [54], epoxy/graphene (4 times) [55], ceramic/graphene (150 times) [45], silane/functionalized GO (130 times) [106], and PMMA/rGO (7 times) [107]. The corrosion protection and durability performance of steel rebar coated (with GO, rGO, and MWCNT mixed to two-part epoxy resin) embedded in concrete was investigated [57]. The average mass loss following accelerated corrosion testing of uncoated steel rebar in concrete saturated with NaCl was 24.5%. In comparison, the mass loss decreases for PE, rGO/CNT, GO/CNT coated rebar to 11.3%, 8.6%, 0.45%, respectively relative to the uncoated steel rebar [57]. These results indicate a direct improvement in corrosion resistance of rGO/CNT coated rebars by 65% and 24%, respectively, compared to uncoated and PE coated rebars. However, the greatest durability performance was observed in the GO/CNT coated rebar where minimal corrosion was observed even after 150 days. More details are provided in Table 1.

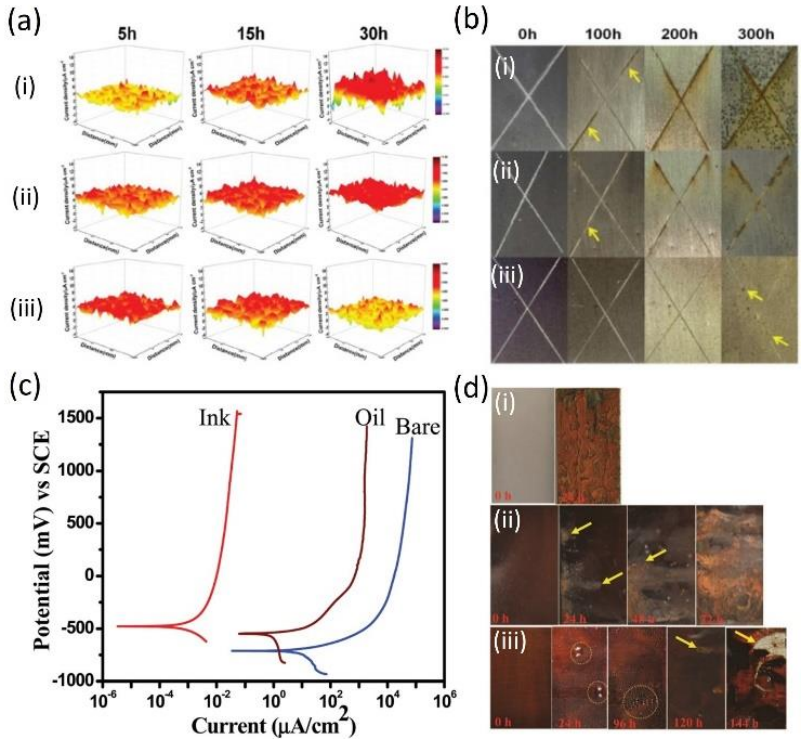

Fig. 9 (a) Scanning vibrating electrode technique maps of current density and (b) digital images of salt spray-test for (i) pure epoxy, (ii) rGO/epoxy and iii) imidazole ion grafted GO/epoxy coatings immersed in a 3.5 wt% NaCl solution. Reproduced with permission from Ref. [51]. Copyright 2018, The Royal Society of Chemistry. (c) Polarization behaviour in 3.5% NaCl aqueous solution and (d) digital images of salt spray test of (i) bare, (ii) oil coated, and (iii) GO ink coated cold-rolled steel. Reproduced with permission from Ref. [52]. Copyright 2015, The Royal Society of Chemistry.

3. Challenges and potential for graphene-based anti-corrosive coating with application to structural steel and rebar for infrastructure application

The inspiring possibilities of graphene-based coating have encouraged major steel producers such as POSCO and Tata Steel to produce anti-corrosive graphene-coated steel [52]. However, industrial manufacturing of graphene-based coating is complicated by misaligned manufacture capability in laboratory and industry in terms of scale, cost, and quality, due to disparate goals, workflows, and standards. Furthermore, the durability and reliability of anti-corrosive coating over long-term usage is

of particular significance for industrial application. In the following subsections, the challenges and potentials of graphene-based anti-corrosive coating on steel progressing in future will be discussed from the perspectives of long-term stability of coatings as well as scalability, cost-effectiveness, quality and environmental sustainability of industrial processing. The discussion is based on the detailed assessment of existing studies on graphene-based coating as summarized in Table 1.

3.1. Long-term stability

The long-term stability is one of the key practical requirements for graphene-based anti-corrosive coating. Specifically, both the mechanical durability (resistance to cracks, wear, fatigue) and environmental durability (stability against humidity, temperature, chemicals) principally rely on the structural integrity and interfacial adherence of the coating.

(1) *Graphene-based monolithic coating:* The defective nature of commercially available graphene and its relative weak adhesion to the rough steel structures limit the long-term anti-corrosion performance for graphene-based monolithic coating. In particular, as shown in Fig. 10a, tilt boundaries usually form during the CVD growth due to the accumulation of dislocations and are considered as linear defects [108]. These defects, on one hand, act as reactive sites to facilitate the localized corrosion of steel in exposed areas. On the other hand, they easily induce the stress concentration and serve as the nucleation centres for cracks (Fig. 10a) [109,110]. Therefore, it is conceivable that grain boundaries render the CVD graphene-based coatings vulnerable to fracture and can lead to catastrophic failure due to the brittleness of graphene [111]. Likewise, other intrinsic defects such as atomic vacancies were found to accelerate the local corrosion owing to an incomplete coverage and consequent galvanic coupling between graphene and metal [112,113]. Such defect-related problems are also inevitable in graphene coatings consisting of micro-sized GNP or GO derived from sonication or liquid exfoliation. In this regard, in-plane defects of graphene can be compensated by vertically stacking multiple graphene layers, which prolongs corrosion pathway and increase the oxidation energy barrier to block the diffusion [114–116].

Apart from the structural integrity, CVD-grown graphene suffers from prominent surface corrugations, as a result of macroscopic roughness of metal substrate and the strain relief attributed to the thermal expansion (Fig. 10b) [117]. Solution-based graphene also easily wrinkles during the processing and deposition [118]. This would lead to interface defects (e.g. buckles) that impair the conformal contact and weaken the adhesion between graphene and the substrate, resulting in the tear and peeling failure of the coating (Fig. 10c) [119,120]. Moreover, buckles can be deemed as micro-channels to allow the intercalation and lateral diffusion of oxygen atoms (Fig. 10d). Considerable strains within buckles further aid to enhance the chemical reactivity and enable an easier etching of graphene, which is detrimental to the long-term anti-corrosion performance [117,121]. Then again, such interfacial issues can be further magnified for structural steels and rebars with highly rough and nonplanar surfaces.

The long-term durability of the coating on the steel is another practical and mechanistic consideration which is affected by it's surrounding environment. Steel rebar in concrete, for example, undergoes extensive mechanical loading [122], friction, shrinkage [123], fatigue [124], extreme weather [125], and potentially harsh chemical exposure (chloride, carbonation, sulphate attack) [126,127] exposure for several decades. Long term corrosion, scratch and abrasion resistance of high precision monolithic coating could be compromised in case of extremely thin and sensitive coating and therefore warrants investigation.

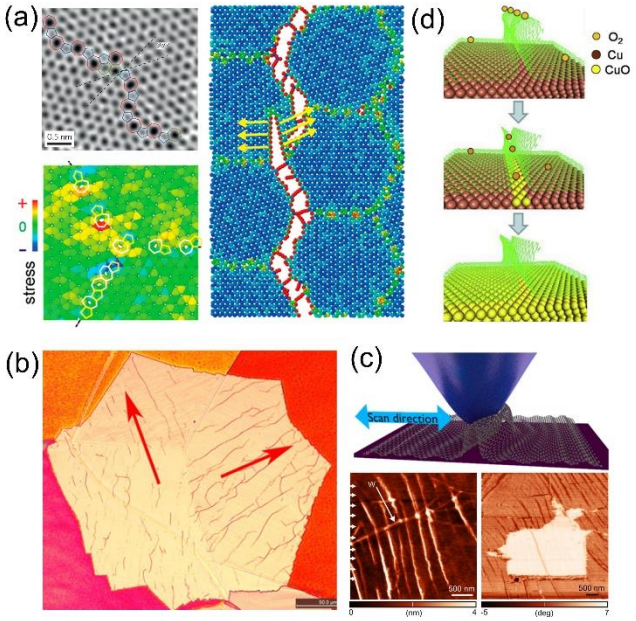

Fig. 10 (a) Grain boundaries in CVD grown polycrystalline graphene with non-uniform stress distributions. Reproduced with permission from Ref. [108]. Copyright 2014, Springer Nature. Reproduced with permission from Ref. [109]. Copyright 2013, American Chemical Society. (b) Optical image of CVD grown graphene after annealing in air, showing distributed wrinkles. Arrows indicate the oxidation lines along the wrinkles. Reproduced with permission from Ref. [117]. Copyright 2014, AIP Publishing. (c) AFM probe scanning induced peeling-off of graphene from the substrate. Reproduced with permission from Ref. [119]. Copyright 2016, Elsevier. Reproduced with permission from Ref. [120]. Copyright 2017, American Chemical Society. (d) Corrosion process of graphene with wrinkles on metal substrate. Reproduced with permission from Ref. [121]. Copyright 2014, Elsevier.

(2) *Graphene-based laminate coating:* As known, thin films and functional coatings can develop significant residual stresses as a pervasive consequence of solid materials processing (Fig. 11a), which is always a major concern in technological applications from a reliability and performance point-of-view [128]. Worst case scenarios might manifest as an isolated crack, connected channelling or an adhesion failure, depending on the material composition and property, stress states and local flaws [129]. Specifically, under the tensile stress, a brittle coating (e.g. atomic layer deposited ceramic coating) may fracture by the growth of cracks through the thickness of the film, while a relatively tougher coating (e.g. spin-cast polymer coating) may fail by delamination along the interface (Fig. 11b). Instead, the failure mechanism associated with a compressive stress in the coating usually involves simultaneous buckling and delamination (Fig. 11c) [130]. Both the cracks and delamination create diffusion paths allowing corrosive species to pass through the thickness or via the coating/metal interface to diminish the barrier function. On the other hand, in service, stresses may arise slowly and cause failure to occur at much lower values compared to theoretical strength. Such a fatigue failure either in crack or adhesive mode may become more severe in the coating with nonuniform stresses, especially for the layer-by-layer assembled laminate coating [98,131]. However, the effective sealing by conformal ceramic or polymer coating offers additional protection for structural steel and rebars. In addition to defect patching, the adhesion to the substrate can also be improved by for example introducing an adhesive polymer layer, which allows application of laminate coating to curved and rough surfaces. Hence, the graphene-based laminate coating is reasonably considered to provide the medium-term corrosion protection for structural steels and rebars.

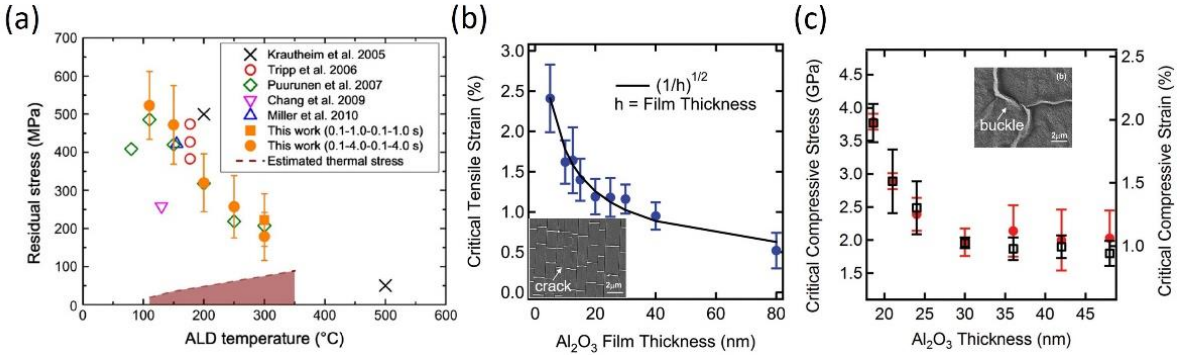

Fig. 11 (a) Summary of residual stress of ALD Al_2O_3 film as function of ALD temperature. Reproduced with permission from Ref. [132]. Copyright 2014, Elsevier. Critical (b) tensile and (c) compressive strains for cracking of Al_2O_3 films as a function of film thickness. The insets are SEM images of cracks under tensile stress and buckles under compressive stress. Reproduced with permission from Ref. [133]. Copyright 2011, AIP Publishing.

(3) *Graphene-based nanocomposite coating:* The primary factor in improving the corrosion resistance in polymer nanocomposites is the tortuosity. Hence, the dispersion and orientation of graphene fillers determines the penetration distance to reach the underlying substrate. However, high surface energy often leads to a high degree of agglomeration of dispersed graphene-based fillers at high content, which tends to impair the tortuous path effect. It has been reported that aggregation of graphene at a high dosage leads to an increasing water permeability through a nanocomposite coating [56,134]. In addition, consequent aggregates show inferior mechanical properties due to the comparatively weak interlayer interactions [135][136]. Hence, GO, rGO and other functionalized graphene are more commonly used for preparation of nanocomposite coating due to the enhanced dispersion and interfacial bonding performance. For example, polydopamine (PDA) has been widely used as a surface modifier due to its abundant catechol and amine groups that may strengthen the interfacial adhesion [137]. It was found that a thin layer of PDA coating could enhance the dispersibility of the PDA-coated GO sheets in organic solvents, providing reinforced barrier property for anticorrosion of graphene-based nanocomposite coating [138]. Furthermore, as an organic polymer, the insulating PDA can bind graphene with metal substrate as glue and inhibit galvanic corrosion simultaneously [139]. The existence of benzene rings in PDA that shares similarities with graphene structure also makes PDA a potential candidate media to heal graphene structure defects [140]. Inspired by mussel and nacre, Zhu et al. designed a bionic epoxy-(graphene-dopamine)-epoxy sandwich composite coating via electrodeposition. They noted that the hydrogen bonding between GO and dopamine, as well as the electrostatic interaction between $–COO^-$ in GO and $–NH^{3+}$ in dopamine assist the self-alignment of graphene parallel to the substrate when subjected to external electric field [141,142]. These highly parallel nanosheets tremendously increase the barrier effect of the coating and prolong the penetration path of the corrosive medium [143]. Generally, the incorporation of graphene into the conventional polymers not only takes advantage of the barrier effect of graphene for protection, but also improves the damage tolerance of the coating. The chemical and thermal stability combined with enhanced mechanical properties further contribute to the mechanical and environmental durability of the nanocomposite coating. The addition of graphene-based nanocomposite coating on steel provides complete coverage of surface by the adherent layer with strong interactions, which plays a vital role in long-term sustainability of the coating [50].

3.2. Scalability

While in-lab fabrication is normally benchtop-scale with low throughput, industrial manufacturing is required to be scaled up, in terms of both the material production and coating process.

(1) *Graphene-based monolithic coating:* Although CVD method has been shown as a relatively scalable process via roll-to-roll operations, it can produce graphene with lateral dimensions in meter size, only on copper [144]. Further production up-scaling is fundamentally limited by the efficiency in the phase change of carbon, as well as the complexity of steel materials required in infrastructures. The steel has a very low catalytic activity for graphene growth and further hinders the large-scale production required for civil infrastructure. In contrast, liquid-phase exfoliation appears more promising in industrial-scale production of graphene. Particularly, high-shear mixing of graphite was demonstrated to give graphene that is many times more efficient than sonication which can be scaled-up to an industrial level [66]. The exfoliation can be achieved in liquid volumes from hundreds of millilitres up to hundreds of litres and beyond. In fact, many companies involved in the carbon business have already established programs on graphene and GO production, and claimed production capabilities of thousands of tonnes/year [145]. In this context, ready access to a coating process that enables the solution-based deposition of graphene layers is required to realize "laboratory to industry" translation. Popular methods used for coatings involve dip coating, spin coating, spray coating, sol-gel approach, in-situ polymerization, and electrophoretic deposition [31]. Among these coating methods, spray coating has proven effective at the industrial scale in terms of size, processing speed and imparted durability, and is not limited to planar substrates [146,147].

(2) *Graphene-based laminate coating:* The assembly techniques for constructing laminate materials, no matter for ALD or layer-by-layer, are mostly limited to small-scale proof-of-concept demonstrations [148]. In principle, ALD is based on the exposure of a surface to a precursor vapour and, therefore, many substrates can be coated simultaneously to increase the scalability. However, such a scalability of ALD technique is more applicable to the semiconductor industry, with limited working area. Furthermore, most abovementioned coating methods lack the industrial scalability except for dip coating and spray coating, yet dip coating is generally time-consuming and labor-intensive. This hinders the industrial implementation of layer-by-layer assembly of graphene-based laminate coating via the combination of different coating methods [149].

(3) *Graphene-based nanocomposite coating:* The preparation method and coating process of the graphene composite anti-corrosive coating can be established based on the traditional coating production process, which has detailed protocols and standard operating procedures in production and shows good controllability and workability in industrial synthesis and applications. In particular, the graphene-based nanocomposite coating methods such as epoxy powder-based fusion-bonded electrostatic coating has been recognized as mature and accessible industrially scalable methods.

3.3. Cost-effectiveness

A successful product design should deliver a balance between working performance and manufacturing cost. Albeit often ignored in academic research, while cost reduction is the priority for industrial development. Therefore, the cost-effectiveness associated with material production and coating process is key to realistically adopting graphene-based coatings and embracing an ambitious industrial shift.

(1) *Graphene-based monolithic coating:* CVD growth method is effective to produce large-scale, high-precision graphene coatings, yet the economic viability may be the principal challenge for the industrial-scale manufacturing of high-quality graphene as the process cost is constrained by the size of substrate, precursor type and energy cost. Comparatively, the use of cheap feedstock and straightforward operation endows liquid-phase exfoliation with higher cost-effectiveness. Additionally, spray coating offers rapid assembly times and is amenable to automation, which is beneficial for cost reduction of graphene-based monolithic coating. Despite the waste issue of dip coating as it typically requires more material than other technologies, especially to submerge large substrates at industrial scales, solutions can be reused for cost saving as long as cross-contamination remains low.

(2) *Graphene-based laminate coating:* Although ALD possesses a number of promising features, it is still technically suffering from low material utilization efficiency and energy-intensive nature [31]. The cost-effectiveness issue associated with the slow deposition rate is critical especially for the industrial production, considering long cycle times and the layer-by-layer nature of the deposition. Particularly, high aspect ratio substrates, such as steel rebars, may require longer time to allow for the precursor gas to disperse into trenches and other three dimensional features [150]. Taking advantage of natural forces (e.g. van der Waals interactions) to form a multilayer, the layer-by-layer assembly requires less investment in manufacturing infrastructure and energy compared with ALD technique. However, resource efficiency is also a major issue for layer-by-layer assembly technologies in coating applications. As only very thin 2D layers are deposited during each growth cycle, a significant amount of waste can be expected [17].

(3) *Graphene-based nanocomposite coating:* Graphene-based nanocomposite coating excels in the relatively lower production costs and sufficient availability. The solution processability of graphene is an advantage for low-cost processing. On the other hand, out of various coating methods, electrostatic coating, sol-gel approach, and in-situ polymerization for preparation of nanocomposites are cost-effective coating methods. As reported, the unit cost of commercial steel and alternative reinforcement rebar for corrosion protection are for steel bar (ASTM A615, grade 60) 0.7 US$/kg [151,152], galvanized coated bar 1.1 US$/kg (converting 1.5 times to the uncoated steel) [153], epoxy coated steel 1.2 US$/kg [152,154], SS (ASTM A955-316L) 5.5 US$/kg [152,154]. Graphene-based coating can be used as an effective coating of steel or to upgrade galvanized and epoxy-based composite coating without much impact on production cost but significant improvement in coating performance.

3.4. Quality

Industrial manufacturing also requires precise process control to assure the quality of graphene and graphene-based coatings, which determines their corrosion protection performance and durability.

(1) *Graphene-based monolithic coating:* The synthesis of graphene has long been a bottleneck for its wide application. While CVD graphene is recognized to have a high quality (i.e. uniform thickness, large area, less defect), solution-based approach never produces 100% monolayer graphene, but a statistical distribution of graphene stacks with lateral dimension limited to a few micrometres [155]. One of the fundamental challenges of graphene production is run-to-run variations in terms of graphene quality, involving defects, homogeneity, thickness and

doping. This is greatly dependent on the quality of the bulk starting materials sold by different vendors. Another remaining challenge would be efficient quality assessment of the liquid exfoliated nanosheets in industrial scale. The significant statistical variation in the quality of graphene and lack of standards are somewhat detrimental to its commercialization [145]. Consequently, the obtained graphene-based monolithic coating is expected to exhibit an inhomogeneous coverage on steel structures.

(2) *Graphene-based laminate coating:* ALD or layer-by-layer assembly techniques provide a more reliable route to fabricate high-quality protective coatings. ALD is known to allow processing dense and homogeneous thin films, by building one mono-atomic layer after another. Such an atomic level control ensures that extremely thin films with high conformality to complex structures can be processed. Furthermore, ALD is exceptionally effective at coating surfaces that exhibit ultra-high aspect ratio topographies (e.g. steel rebar), providing a robust coating with high-quality interfaces. Such advantages of precise control of thickness and composition as well as nanoscale interface engineering can also be found in other solution-processing layer-by-layer assembly techniques.

(3) *Graphene-based nanocomposite coating:* The quality of raw graphite and liquid-exfoliated graphene and chemically synthesized functionalized graphene also influences the quality of graphene-based nanocomposite. Parameters such as the flake size thickness (related to volume concentration), functionalization, and dispersion state play a key role in the tortuous effect for protection efficiency. Meanwhile, the dispersion issues have been deemed as roadblocks on the journey of manufacturing of high-performance nanocomposites. While postprocessing may be effective to alleviate these issues by additional procedures, the overall quality of nanocomposite coating can be guaranteed by the standard manufacturing process using industrial-scale equipment in a streamlined manner.

3.5. Environmental sustainability

Key issues such as environmental sustainability deserves special attention during the practical applications. Many of the potential environmental impacts that can result from the industrial process are related to chemical reactions that take place within a facility.

(1) *Graphene-based monolithic coating:* CVD method is suitable for high precision graphene coating, yet there are hazard issues due to the use of toxic chemical precursors and generation of reactions gas or liquid by-products during the deposition process. Besides the material use and emission generations, energy consumption of CVD is another concern for environmental justifications. To increase the material utilization efficiency and reduce the amount of waste, optimization of the reaction process through establishing an optimal precursor supply pattern is required. Likewise, the chemical reduction of GO mostly includes highly hazardous reducing agents that are dangerous to the environment. Nevertheless, green synthesis strategies of graphene have been developed recently by using bio-materials or non-toxic chemicals as reducing agents, which are eco-friendly [156].

(2) *Graphene-based laminate coating:* The principal by-products for ALD coating process is methane, a major greenhouse gas and has a global warming potential 25 times that of carbon dioxide [157]. The material utilization efficiencies of precursors are reported below 20% in ALD operations, which is mainly due to the limitation by the smaller working area compared

with the ALD reactor. In contrast, layer-by-layer assembly is considered as an environmentally friendly process to ensure sustainable consumption and production of film materials.

(3) *Graphene-based nanocomposite coating:* Owing to growing environmental concerns on emission of organic volatiles, waterborne polyurethane (WPU) has become an attractive material for coating applications. To increase environmental friendliness and sustainability, water is a tempting choice as an exfoliation medium, especially for WPU/graphene nanocomposites. In addition, sustainable noncovalent modifiers are preferred to alleviate the dispersion issues. Recently, graphene-based WPU nanocomposite coating has been prepared by using a green, aqueous-only production route from graphite, showing great prospect in the application of corrosion prevention [158].

By comparison of five key indicators for the present assessment on three different graphene-based coatings, a radar plot is drawn in Fig. 12 whereby a preference score (1 = low, 2 = medium and 3 = high) is assigned to each key indicator. The most promising graphene-based coating for commercialization in anti-corrosion applications would be indicated by the highest total score. Based on the ranking in this study, considering the comprehensive performance, graphene-based nanocomposite coating exhibits the strongest potential for long-term stability, scalability, cost-effectiveness, quality, and environmental sustainability, over to the other two types of graphene-based coatings considered in this study, and therefore is optimal option for further research regarding anti-corrosive performance of steel rebars.

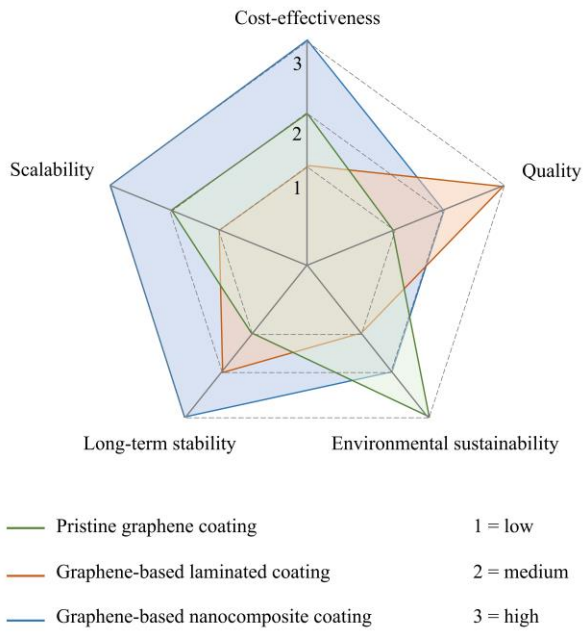

Fig. 12 A radar plot showing a comparison of comprehensive performance among three different graphene-based coatings.

4. Future prospects

Corrosion of structural steel and reinforcing steel rebar in concrete is a major issue for the stability, integrity and service life of civil infrastructure. Corrosion of steel rebar in concrete, for example, can lead to the cracking of concrete, spalling, and staining of the RCC infrastructure. Epoxy resins can be adopted as anti-corrosive coatings in structural steel and rebar due to its crosslinking structures which provide high adhesion and chemical resistance. However, epoxy-coated steel is brittle [57] and have undergo pitting corrosion. Epoxy-coated steel rebar failure in a reinforced concrete structure was

identified in the early 1990s [159]. Another current industry practice is galvanized steel coated with a layer of zinc, which is reported to have conflicting performance. One study reported that the threshold level for initiating corrosion in galvanized rebar is 4 to 10 times higher than the threshold level for HR steel rebar while another study reported that galvanized rebar have a slightly improved anti-corrosion performance in severe chloride environments [160].

In comparison, graphene based anti-corrosive coating on steel rebar are examined. Nano layer thick (single to multi-layer) pristine graphene coated steel [38–40,161] are reported to have up to 45 times lower corrosion rate [38] compared to bare SS steel. Graphene composite based coating on steel with 0.8 to 110 μm uniform thickness [19,49,51,52,55] was reported to reduce the corrosion rate up to 10,000 times [53] compared to that of bare CR steel. The durability performance of steel rebar in concrete show a significant improvement after multilayer electrostatic GO coating [44], and GO/CNT/epoxy based composite coating [57]. The addition of graphene based coating on steel as well as complete coverage of surface by the adherent layer plays important role for long-term durability of the coating [50]. Future research direction of graphene-based anti-corrosive coating and other 2D materials-based coating are presented in the section that follows.

4.1. Graphene-based smart anti-corrosive coatings

Advancement in nanotechnology and graphene-based anticorrosive coating is expected to pave a way for the developments of effective multifunctional construction materials with smart properties. Based on the assessment in this study, while graphene-based nanocomposite coating outperforms monolithic and laminate coating in view of long-term protection, there remain some practical questions to be solved. The long-term persistence of nanocomposite coating is still threatened by unexpected mechanical damage due to repeated wear and tear and accidental cutting or scratching. A polymer's durability and stability of the graphene based composite system warrants attention, particularly in a high alkaline environment [44]. Other durability factors of concrete besides NaCl attack on steel rebar, such as sulfate attack and carbonation [162] impact on graphene coated steel need in-depth investigation. Development of smart composite coatings with self-sensing [163], and self-healing [164,165], multifunctional capability (sensing, self-healing, repair, and restoration of functions) will be a future direction.

To this end, the superior physicochemical properties of graphene enable it to play various functional roles in different healing mechanisms, both intrinsic and extrinsic. Self-healing in construction materials field referred to any process the materials recovers its performance after initial damage, such as strength, density and permeability [166]. In terms of the intrinsic healing mechanism, where reversible chemical bonds are dissociated and reconstructed by external stimulation to repair the material, graphene can not only act as the centre of energy transfer and conversion to improve the efficiency of energy transfer, but also carry functional groups to facilitate the construction of reversible chemical bonds [165]. Moreover, the thermal conductivity and photothermal/microwave conversion ability of graphene combined afford the possibility for the multilevel healing in coating. On the other hand, for the extrinsic healing coating, graphene is deemed as a promising inorganic nano-container to carry inhibitor molecules, due to its large specific surface area and abundant active absorption sites on the surface. The graphene-based nanocontainers possess lamellar morphology and can be applied to steel rebar ultra-thin coatings with smart functionalities without affecting the stability. Both intrinsic and extrinsic self-healing mechanisms represents the future development trend of self-healing graphene-based composite anticorrosive coatings.

In addition, flexible graphene-based thin layer shows the ability of high sensitivity which can be applied to measure electrical signals generated from small deformation [163], providing a viable means to strain sensors smart coating on steel rebar. The graphene-based smart coated sensors with ultrafast response could capture the time-dependent mechanical response through the coated steel rebar in the infrastructure. The combination of thin coating, higher efficiency in anti-corrosion properties and possibilities of these smart properties is expected to revolutionize steel rebar and structural steel performance in the civil infrastructure industry.

4.2. Anti-corrosive coating of 2D materials beyond graphene

Graphene has been studied most for coating application among the other dense 2D nanostructure materials, such as hexagonal boron nitride (hBN), molybdenum disulfide (MoS_2), and molybdenum diselenide ($MoSe_2$), which show promising scope to develop nanoscale coating on steel with several tuneable properties. Despite the great potential of graphene as anti-corrosive coatings, it is cathodic to most metals and can promote corrosion at exposed graphene–metal interfaces owing to the galvanic coupling. In that aspect, functionalization of graphene with nonconductive properties such as GO, and the conjugation of all forms of graphene with insolating polymer and other 2D nanomaterials are more suitable solutions for mitigating this issue and develop effective coating in steel surface.

In depth investigation on other 2D materials beyond graphene such as hBN, MoS_2, and $MoSe_2$ is required to explore for the development of next generation smart coatings. Hexagonal boron nitride (hBN), for example, is a layered 2D electrical insulator (also called “white graphene”), can well resolve the galvanic corrosion issues and has become an ideal coating material against corrosion. Considering the similar hexagonal structure as graphene, hBN is also expected to have a high impermeability and provide the barrier protection. In addition, it was reported that hBN coating could substantially reduce the oxidation of metallic surfaces at extremely high temperatures owing to its exceptional thermal and chemical stabilities [167]. Even under a range of abiotic (sulfuric acid and sodium sulfide) and biotic (sulfate-reducing bacteria medium) sulfuric environments, atomically thin hBN layers can still effectively inhibit the corrosion of the underlying copper [168]. Furthermore, hBN can be composited with polymers to make hybrid paint, which was found to provide excellent protection of stainless steels from marine corrosion when tested under a simulated seawater media [48]. Recently, the direct growth of large-area, high-quality, uniform, and continuous h-BN coating on industry-relevant SS304 surfaces has been realized by magnetic sputtering method, which may accelerate the progress of hBN nanofilm applications in the industry [169]. It is envisaged that conformal coatings based on 2D materials and their heterostructures will afford appealing routes to protect metals against aggressive environments including thermal oxidation, microbial corrosion, and atmospheric corrosion [170,171]. Add to that, the functionalized graphene could be combined with hBN to produce a thin layer coating for steel with cost effective and multifunctional properties.

5. Conclusions

Reinforcement in concrete infrastructure exposed to corrosive environment is required to have high anti-corrosive properties. Conventional epoxy and zinc coated steel rebar, in that aspect, have increasing demand in the construction industry despite of their limitations and controversial performance in many cases. Graphene-based anti-corrosive coating could be an effective solution in the development of next generation steel rebar industry.

This review presents the progress on multiple sorts of graphene in the forms of monolithic, laminate, and nanocomposite anti-corrosive coatings with a focus on steel applications. A clear picture of each coating process is provided in a chronological discussion of anti-corrosion mechanism, preparation and coating methods, and anti-corrosion performance. Despite the significant potential of graphene as protective coatings, this study identifies the roadblocks and challenges that need to be addressed before reaching market. The review also critically compares the three different graphene-based coating systems with respect to long-term stability, scalability, cost-effectiveness, quality, and environmental sustainability, leading to proposed recommendations on the future of research in the field of steel rebar coating for civil infrastructure application. To summarize the key findings:

Graphene-based monolithic coating can be thinnest possible coating (nanoscale) with ultrahigh fracture strength and fatigue life. The anti-corrosion mechanism lies in its impermeability to gases and liquids. However, structural defects are inevitable for no matter CVD grown or solution processed graphene films, which accelerate the corrosion of metals in the long term. The brittleness of graphene also makes it vulnerable to scratches or cracks, easily resulting in an incomplete coating coverage on the substrate surface. Furthermore, intrinsic corrugations and weak van der Waals interactions enable corrosive molecules to diffuse, intercalate and penetrate at the interface, accounting for the short-term protection as well.

In this regard, graphene-based laminate coatings being the combination of graphene with polymer or ceramic in hybrid coatings provides a thicker and more robust corrosion barrier for the metal surface. The layer-by-layer assembled structure with precise control of composition and thickness would be more compact and ordered, efficiently suppressing the cohesive failure and affording a complete sealing of metal surfaces. Furthermore, additional insulating protective layer aids to break the galvanic coupling between graphene and metal substrate, which benefits the long-term anti-corrosion performance to meet the industrial requirements. Nevertheless, the major concerns of the steel industry over using graphene-based laminate as a corrosion inhibitor are related to the technical difficulties in layer-by-layer assembly. For example, the demands of high throughput and quality for industrial-scale mechanical transfer and stacking of graphene/polymer coating have not been fulfilled. Residual stress raises critical issues in ALD layer that are detrimental to the stability and reliability of the laminate coating. More concerns regarding the application of steel rebar with rough, nonuniform surfaces need to be addressed.

Generally, an optimal route to overcome many of these issues is to incorporate graphene into polymers to produce the nanocomposite coating. Compared to graphene-based monolithic and laminate coating, graphene-based nanocomposite coating, can be versatile, cost-effective, easily scalable with consistent quality, much thicker, which is an efficient solution for steel surface corrosion protection. The embedded graphene not only inhibits the penetration of corrosive substances (torturous effect), but also retards the propagation of cracks (toughening mechanism). The resulting composite coating also leverage the advantages of a polymer coating, such as the scratch-resistance and conformal adherence to the substrate. The mature technology, detailed protocols and standard operating procedures for polymer manufacturing and coating could be transferred to the production of nanocomposite coatings on steel. In addition, considering the multifunctionality of graphene and extensive library of polymer matrix, the nanocomposite coating will hold enormous potential in adaptation to a broad spectrum of applications. To fully unleash the potential, strategies to increase the dispersion, interface bonding, and alignment of graphene in polymer matrix are required. The concentration of graphene in the polymer nanocomposite should be selected considering the fact that the agglomeration effect of nanomaterials could occurs at low filler concentration compromising the excellent water barrier properties. More efforts should be directed toward developing green and environmentally friendly modification methods, to minimize pollutions and health hazards. In addition, from the scientific perspective, optimized design

of nanocomposite coating requires deeper understanding of the specific materials and interfacial interactions, especially detailed structure-property-function relationships. Computational tools are hence necessary to capture the physics and chemistry of the nanomaterials as well as their interfaces during the deformation and failure process. Predictive multiscale modelling can leverage quantum mechanics calculations (e.g. density functional theory) to describe the electronic structure and coupling of individual building blocks, as well as larger scale models to understand the structure of the materials up to the continuum level. The integration of theoretical modelling, numerical simulations and experimentation is instrumental to develop a multiscale structure-property paradigm that guides an accurate design of high-performance nanocomposite coatings.

CRediT author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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