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Communication

Layer-by-layer stacked graphene nanocoatings by Marangoni self-assembly for corrosion protection of stainless steel



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ABSTRACT

Graphene nanosheets are widely used in anti-corrosion polymeric coating as filler, owing to the excellent electrochemical inertness and barrier property. However, as the arrangement of graphene nanosheets is difficult to form a perfect layered structure, polymeric coating with graphene nanosheets usually needs micron-scale thickness to ensure the enhancement of corrosion protection. In this work, layer-by-layer stacked graphene nanocoatings were fabricated on stainless steel by self-assembly based on Marangoni effect. The anti-corrosion property of graphene coatings were studied through Tafel polarization curves, electrochemical impedance spectroscopy and accelerated corrosion test with extra applied voltage. The self corrosion current density of optimized three-layered graphene coated sample was one quarter of that of bare stainless steel. And the self corrosion potential of optimized sample is increased to -0.045 V. According to the results, graphene nanocoatings composed of layered nanosheets exhibits good anti-corrosion property. Besides, the self-assembly method provide a promising approach to make layered-structure coating for other researches about 2D material nanosheets.

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Graphene has attracted lots of attentions in many aspects since its first preparation in 2004 [1]. Over the past twenty years, numerous unique physical properties of graphene have been reported, such as high thermal and electrical conductivities [2,3],

ultrahigh electron mobility [4], high specific surface area [5] and good mechanical strength [6]. Besides, graphene is regarded as a perfect atomic-scale barrier that can block small molecule gases (oxygen and helium) and liquids (water) [7,8], due to its impermeable nature based on two dimensional honeycomb structure and strong sp^2 carbon-carbon bindings. Additionally, graphene is considered inert in the environment of electrochemical reactions [9,10], which makes graphene a potential coating material for corrosion inhibiting of the metal substrates.

In order to prepare a graphene based anti-corrosion coating, the synthesis of graphene by chemical vapor deposition (CVD) with

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catalytic metals is an extensively used method [11,12]. Early researches indicated that CVD graphene has good horizontal layer structure and low defects, which can inhibit the oxidation on metal surface both in theory and practice [13,14]. Later on, the counterview appeared, which demonstrated that the metal oxidation will aggravate at tiny defects and wrinkles of graphene [15]. And numerous works demonstrated that CVD graphene showed excellent performance to barrier ions for metal in a corrosive environment. For example, Prasai *et al.* reported that Ni coated with 4 layers of transferred CVD graphene is corroded in Na_2SO_4 solution in a rate 4 times slower than that of bare nickel [16]. Kirkland *et al.* found that single-layer graphene would reduce the anodic dissolution of nickel and the cathodic reduction of copper for more than one-order of magnitude in NaCl solution [17]. Raman *et al.* investigated the corrosion of CVD graphene coated copper in NaCl solution [18], and demonstrated that the impedance of coated copper is two orders of magnitude higher compared to uncoated copper. Although CVD method can obtain high-quality graphene as the anti-corrosion coating, it still has several shortcomings. One of them is that CVD graphene has the nanoscale thickness, which is not suitable for the micron-scale roughness of polished metal substrate in practice [15]. Meanwhile, the defects and structural deterioration of CVD graphene is inevitable in transferring process which degrades anti-corrosion performance. In order to solve the problem, complicated repeated transferring is needed, which restricts available conditions [16]. At present, CVD graphene anti-corrosion coating is still far from practical application.

Using polymer matrix coating and paints incorporated with graphene nanosheets as anti-corrosion filler is an easier and more repeatable way [19]. Graphene nanosheets have higher surface area than conventional barrier pigments, which provides better protection [20]. As a well-accepted mechanism, dispersed graphene nanosheets in polymer matrix increase the invasion route of corrosive ions, leading to that coating can passivate substrate more effectively [21]. Chang *et al.* developed graphene/epoxy composites with hydrophobic surfaces as corrosion inhibitor on cold-rolled steel, achieving an increase of 0.4 V corrosion potential [22]. Chang *et al.* reported graphene/polyaniline composites as protective layer on bare steel, which displayed good barrier property against water and oxygen [23].

Comparing above two approaches, CVD graphene coating is able to achieve good barrier performance with thickness of several nanometers due to its few-defect and well-arranged layered structure. While polymeric coating reinforced by graphene nanosheets usually needs tens of microns thickness, owing to that arrangement of graphene nanosheets is difficult to be controlled. Therefore, it is significant to find an effective method to adjust the arrangement of graphene nanosheets [24–27], which can make coating as thin as possible and present the shielding performance closed to CVD graphene. In this work, an ultrathin film composed of layer-by-layer assembled graphene sheets formed on water surface based on Marangoni effects was prepared and then transferred onto stainless steel. The anti-corrosion property of this polymer-free coating was investigated, while with the optimized three-layer graphene coating, the corrosion potential increased by -0.15 V and corrosion current density reduced to 1/4 of the original value of stainless steel. As a barrier, multilayer graphene coating is able to prevent stainless steel from pitting corrosion in high chloride concentration environment, even under the applied voltage of electrochemical accelerated test.

The ultrathin layer-by-layer graphene coatings on stainless steel (SS) were fabricated through Marangoni self-assembly of graphene nanosheets. The concentration of graphene/alcohol dispersion was adjusted into 0.1 mg/mL. In order to avoid aggregation of graphene nanosheets, the dispersion was ultrasonicated for 1 h before using. 0.1 mg/mL graphene alcohol dispersion was carefully added onto the surface of water in a steady inflow. Since the surface tension of alcohol is smaller than water, once a drop of graphene alcohol dispersion touches the water surface, the gradient of surface tension impels alcohol and graphene sheets to spread rapidly on the horizontal direction, which is Marangoni effect [28,29]. Due to the intrinsic hydrophobicity, graphene sheets floated on the water surface, collided and finally self-assembled into a uniform, single-sheet-thick graphene film. Self-assembled graphene coating on the water was carefully fished onto treated SS substrates, followed by drying at 60 °C in atmosphere. Graphene coating with different layer numbers can be facily formed by repeating above process (Fig. 1a). The photograph of SS and samples with 1, 2 and 3 coating times (named 1 LG, 2 LG and 3 LG) are shown in Fig. 1b. The graphene

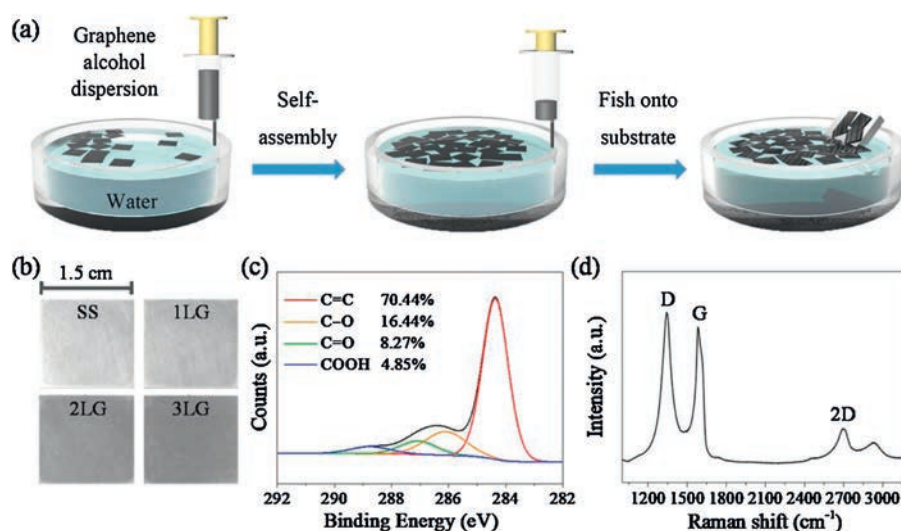


Fig. 1. (a) Scheme of preparation process of Marangoni self-assembled graphene coating. (b) Photos of SS, 1 LG, 2 LG and 3 LG samples. (c) XPS C 1s spectrum and (d) Raman spectrum of graphene sheets.

coating is uniform in centimeter-scale with a transmittance of 89% of each layer at visible light region.

Analyses of XPS and Raman spectroscopy were first carried out in order to identify the quality of graphene sheets. As shown in Fig. 1c, the XPS C 1s spectrum of graphene sheets can be fitted into four peaks, including C=C bond (284.4 eV), C—O bond (286.1 eV), C=O bond (287.1 eV) and —COOH (288.7 eV). The ratio of oxygen-containing groups of graphene was about 29.6%, which indicated that the quality of this graphene was close to reduced graphene oxide [30]. In Raman spectrum (Fig. 1d) of graphene, a prominent D-band ($\approx 1353\text{ cm}^{-1}$), a large G-band ($\approx 1585\text{ cm}^{-1}$) and a small 2D-band ($\approx 2700\text{ cm}^{-1}$) were observed [30]. Accordingly, the graphene sheets were multi-layer graphene with some defects, which is similar to those graphene commonly used as anti-corrosion coating filler [31].

The morphology of graphene coatings was investigated through SEM observation. Note that samples with different coating layers were prepared on smooth SiO_2/Si substrate for better characterization. As shown in Figs. 2a–c, it can be observed that graphene coating was composed of numerous graphene flakes, which have an average lateral size of $0.85 \pm 0.48\ \mu\text{m}$. When repeating the transfer process, the upper graphene coating would partially fill the spaces between graphene sheets of the lower coating. Based on this layer-by-layer assembly method, graphene sheets can almost cover the surface of substrate after 3 times. The coverage ratio of the graphene coating was estimated as 82.8%, 94.3% and 98.6% for 1LG, 2LG and 3LG, with an average coating thickness of 1LG, 2LG and 3LG was 2.8 nm, 6.9 nm, and 12.7 nm, respectively (Fig. 2d). Note that the thickness of coating is measured by a spectroscopic ellipsometer (M-2000DI, J.A. Woollam Co., Inc., USA) as an average thickness. The thickness increased evenly with the number of coating layer, demonstrating that the proposed self-assembly approach through Marangoni effect is a promising method to fabricate uniform nanometer-thick coating.

The anti-corrosion performance of our fabricated ultrathin graphene coatings on the SS surface was investigated by

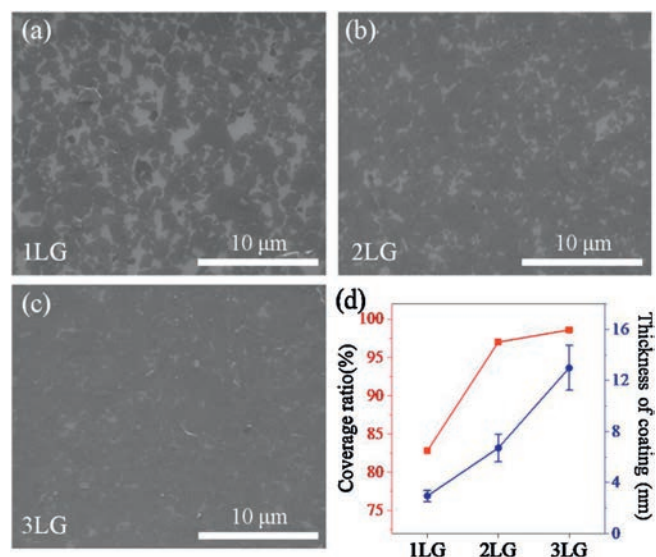


Fig. 2. (a–c) SEM pictures of 1LG, 2LG and 3LG coatings. (d) Coverage ratio and thickness of different coatings.

potentiodynamic polarization tests. All the samples were tested in 3.5 wt% NaCl solution after 1 h immersion. The Tafel curves are shown in Fig. 3a. The bare SS without coating showed the lowest corrosion potential (E_{corr}) at -0.192 V . With an increase of the layer number of graphene coating, E_{corr} gradually increased to -0.045 V . It demonstrated that in thermodynamics, SS became difficult to corrode with the assistance of layer-by-layer stacked graphene coating, due to the excellent shielding property of graphene. The free corrosion current density (j_{corr}) of samples was evaluated by Tafel extrapolation method for studying the corrosion kinetics and the results are shown in Fig. 3b. Comparing to j_{corr} of SS ($1.64 \times 10^{-7}\text{ A/cm}^2$), the j_{corr} of 1LG samples is abnormally

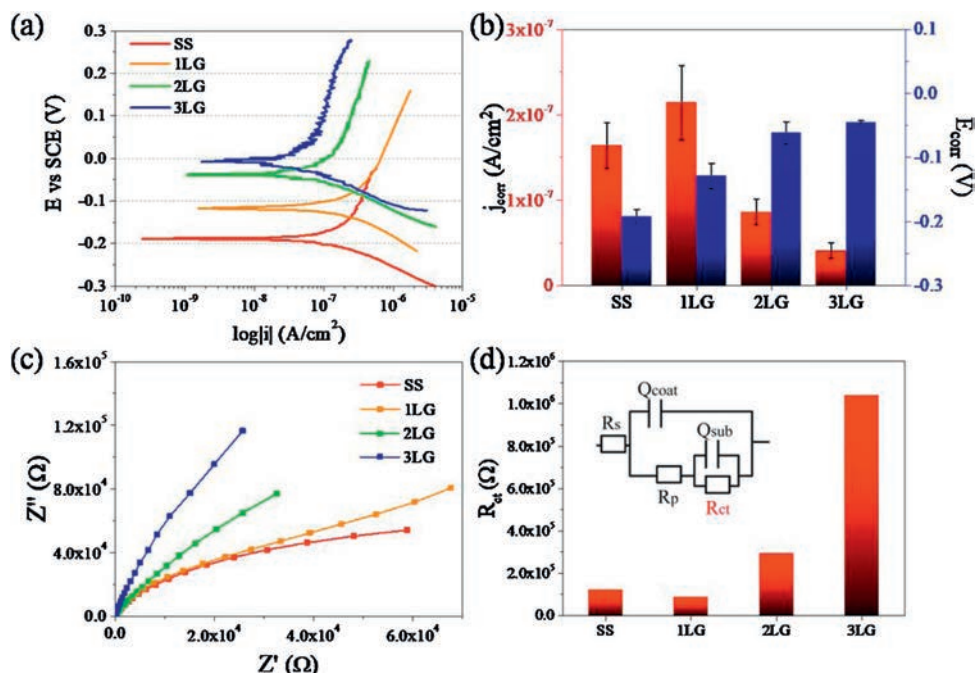


Fig. 3. (a) Potentiodynamic polarization curves of the SS, 1LG, 2LG and 3LG samples; (b) Bar chart of corrosion current density (j_{corr}) and corrosion potential (E_{corr}) evaluated from (a). (c) Nyquist plots of SS, 1LG, 2LG and 3LG samples. (d) Fitted R_{ct} value of samples (Inset: equivalent electrical circuit).

increased to 2.14×10^{-7} A/cm², which means the corrosion rate of 1 LG will be faster than SS. This phenomenon can be attributed to those edges of graphene sheets in 1 LG coating, which created lots of exposed Fe–C sites.

At these sites, corrosion of Fe atoms is accelerated due to the formation of Fe–C galvanic cell in NaCl solution. In 2 LG and 3 LG samples, as the coverage ratio is increased, exposed Fe–C sites are declined and j_{corr} decreased to 53% and 25% comparing to those of SS, demonstrating the corrosion inhibition of the coating composed of graphene sheets.

Electrochemical impedance spectroscopy (EIS) is executed to analyze the interfacial condition of graphene coating and the SS substrate, and the Nyquist plots of SS and graphene coated samples are shown in Fig. 3c. In Nyquist plots, larger radius of impedance arc reflects the greater interfacial resistance of the coatings. To further investigate the corrosion mechanism, the equivalent electrical circuit $R_s(Q_{\text{coat}}(R_p(Q_{\text{sub}}R_{\text{ct}})))$ was selected to fit the EIS data. The result of fitting parameters is shown in Table 1. Among these parameters, R_{ct} is on behalf of the charge transfer resistance at the coating/substrate interface, which can reflect the corrosion reaction rate. As shown in Fig. 3d, it is obvious that the R_{ct} value had a sequence of 1 LG < SS < 2 LG < 3 LG, which is corresponding to the variation of j_{corr} . With an increase of coating times, the obvious increase of R_{ct} can be attributed to the electrochemical inertia of layer-by-layer stacking graphene structure fabricated by Marangoni self-assembly. According to above results, this polymer-free nano-thick graphene coating exhibits protection capability, which can block corrosion factors as the physical barrier for SS substrates.

In order to investigate the real conditions for practical applications, we analyzed electrolytes and sample surface after accelerated corrosion test which could offer the information of corrosion damage. A high bias voltage (0.4 V) was applied between different samples (as working electrode) and reference electrode in room temperature. Under 0.4 V bias, the pitting corrosion is the main mode on SS surface. Therefore, a pair of half-reactions was taken place during the corrosion [32]:



As the reactions continue, iron element would escape from the substrates and enter into electrolyte, resulting in an increase of total amount of iron element in electrolyte. The product of these

Table 1

The fitting parameters of EIS for the SS, 1 LG, 2 LG and 3 LG samples.

Sample	R_s (Ω)	C_{coat} (F)	n_{coat}	R_p (Ω)	C_{sub} (F)	n_{sub}	R_{ct} (Ω)
SS	14.64	N.A.	N.A.	N.A.	1.01×10^{-4}	0.890	1.18×10^5
1 LG	21.72	5.26×10^{-6}	0.919	10.21	1.55×10^{-5}	0.958	8.90×10^4
2 LG	16.63	1.07×10^{-5}	0.864	7.77	4.90×10^{-5}	0.953	2.95×10^5
3 LG	17.30	2.60×10^{-5}	0.844	2.618	8.11×10^{-5}	0.963	1.04×10^6

two reactions is Fe(OH)₂, which is then automatically oxidized to form insoluble FeOOH in water. Electrolytes were all re-collected after accelerated corrosion tests. Before the following characterizations, each electrolyte (5 mL) was pretreated by hydrochloric acid, to ensure that all FeOOH could transfer to Fe³⁺. The concentration of Fe³⁺ was identified by inductive coupled plasma (ICP) emission spectrometer. As shown in Fig. 4a, the Fe³⁺ concentration dissolved from SS, 1 LG, 2 LG, respectively, is in a range of 4.5–6.0 mmol/L, while that of 3 LG is about 2.8 mmol/L. We demonstrated that the three-layer graphene coatings with less than 14 nm thickness could reduce 55% corrosion damage, exhibiting an excellent shielding performance. After accelerated corrosion tests, lots of pitting holes were formed due to the dissolution of iron (Figs. 4b–e). Through counting holes larger than 20 μm in diameter, the density of pitting holes on sample surface decreased in the following order: 1 LG > SS > 2 LG > 3 LG. The results suggest the structural failure of material under serious corrosion condition, which matched well with the results of potentiodynamic polarization tests and EIS tests. In conclusion, the results of electrochemical tests demonstrated that self-assembly graphene coating can help to protect SS from corrosion.

In this work, layer-by-layer stacked graphene coatings for anti-corrosion were fabricated by Marangoni effect self-assembly. The morphology and anti-corrosion properties of coatings were characterized systematically. Comparing to bare stainless steel, well-covered samples with three-layer graphene coating can achieve a corrosion potential increase of 0.15 V and a corrosion current density decrease of 1.23×10^{-7} A/cm². Excellent barrier performance of optimized graphene coating with only 13 nm thickness was also proved, achieving 55% off of corrosion comparing to bare SS. Moreover, this work may provide a novel idea toward the measurement of anti-corrosion property for 2D-material nanosheets without polymer matrix.

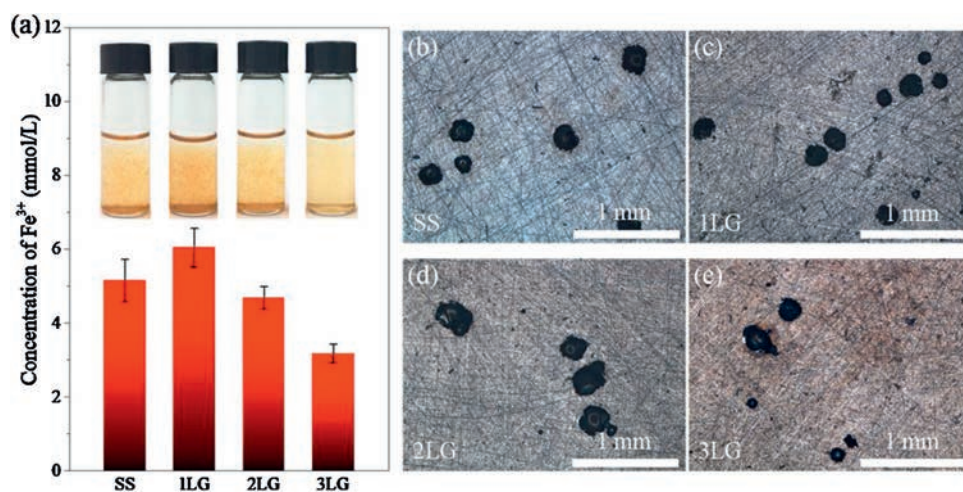


Fig. 4. (a) Photos of electrolytes after accelerated corrosion test and concentration of Fe³⁺ in different electrolytes measured by ICP. (b–e) Surface condition of SS and LG samples after accelerated tests.

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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