



# Inhibitor or promoter: Insights on the corrosion evolution in a graphene protected surface



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## ARTICLE INFO

### Article history:

Received 1 August 2017

Received in revised form

27 September 2017

Accepted 7 October 2017

Available online 8 October 2017

## ABSTRACT

Corrosion is a fundamental electrochemical problem that results in significant material degradation and failure and affects the performance of many engineering components. Additionally, corrosion associated material losses often produce contamination of surrounding media. Discovery of two-dimensional (2D) materials has opened a venue for multiple attempts in designing atomically thin anticorrosive coatings for prevention and control of corrosion propagation in metals. It was shown that graphene, for example, when uniformly coating a metal surface can inhibit corrosion-initiated degradation of copper and nickel. Here we demonstrate that graphene plays an important role in oxidation-based corrosion processes. Non-uniform graphene coverage has an enormous effect on corrosion protection and may lead even to acceleration of corrosion. We demonstrate that when immersed in sodium chloride solution the exposed edges of graphene become the centers for iron oxidation and propagation. Beneficially, high mechanical stability of graphene substantially eliminates metal losses and leads to only oxidation-based mass increase. Our extensive characterization analysis indicates the reason for this is high concentrations of trapped chlorine atoms on the edge of detached from the surface graphene flake. Chlorine increases metal dissolution and results in significant oxidation sites along the graphene edge line.

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## 1. Introduction

Material reduction/oxidation reaction in an oxygen-rich environment is indicative of the corrosion propagation process [1–4], typically observed for corrosive metals, such as iron, nickel, and copper. Corrosion is further accelerated in electrochemically reactive media (such as for example salted water) and results in dissolution of metal through the interaction of metal cations with oxygen or halide ions (e.g., fluoride, chlorine) [5]. Introducing initial cracks and defects on the metallic surface largely impacts the rates of corrosion propagation by accelerating further material degradation [6]. In addition to material properties deterioration, corrosion causes contamination of the surrounding media by lost degraded materials [5,7]. To limit corrosion propagation, current technologies on metal usage in corrosive environments rely heavily on passive metal oxide layers, which substantially modify and limit such important characteristics of metals as mechanical strength

and electrical conductivity [8,9]; and affect surface interactions with the surrounding media.

To eliminate the problem of the passive layer, 2D carbon materials have been explored as atomically thin coating films for their potential to protect the underlying metal substrate from corrosion [10–13]. Specifically, graphene, a miracle material with an enormous number of potential applications [14,15], has been tested for corrosion inhibition based on its high chemical stability [16], impermeability to gasses [17], and excellent mechanical properties [18]. Recent studies have shown that graphene when deposited on the surface of refined metals such as copper and nickel can act as a protective layer against corrosion processes in an aerated Na<sub>2</sub>SO<sub>4</sub> solution [19] or in a hydrogen peroxide solution [20]. Graphene also helped to prevent steel corrosion during sliding in a macroscale pin-on-disk experiment [21,22]. The observed effect of anticorrosion protection is believed to originate from the graphene's impermeability to the liquids and gasses [23,24], which leads to insulating the underlying material from exposure to corrosive species. Note that in the reported earlier studies, graphene mostly forms uniform coverage of the underlying substrate during direct chemical vapor deposition (CVD) or in the process of sliding.

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Though, Prasai et al. have indicated the presence of corrosion in an unprotected area where the cracks in graphene are formed [19], the impact of the defects has been considered minimal and overall neglected. Additional studies on the graphene as an antioxidation barrier for a copper surface indicated deterioration of the graphene's anticorrosion properties with time [25]. Conductive graphene helps in facilitating electrochemical reaction across the surface, thus leading to more continuous corrosion processes in ambient environment. Passivation of the graphene defects with aluminum oxide deposited by Atomic Layer Deposition (ALD) [26] or encapsulation of reduced graphene oxide with (3-aminopropyl)triethoxysilane (APTES) [27] helped to increase anticorrosion resistance of atomically thin graphene layers.

In this paper, by using the Quartz Crystal Microbalance (QCM) technique [28] in NaCl solution, we explore degradation processes of a highly corrosive metal, iron, when the metal surface is non-uniformly covered with graphene. QCM allows to monitor even smallest changes in materials' chemistry and structure and interactions with surrounding media, when the material of interest is deposited on the QCM electrode's surface [29]. We demonstrate that corrosion process becomes very selective to the cracks or edges of transferred-on-the-metal single layer CVD graphene and may result in overall higher degradation of materials with the graphene coating on them. However, graphene in this case keeps the iron oxide material together and cease any losses of the material. While unprotected iron oxide starts to lose mass, the material gain due to oxidation in graphene protected iron stops only when it penetrates completely all the way down in the material. However, when the number of the graphene edges is large, it accelerates corrosion processes without ability to keep oxidized material together. The effect becomes even more prominent when graphene is deposited from a solution in the form of sporadic flakes, providing only 50–60% coverage of the surface.

## 2. Experimental procedure

### 2.1. Sample preparation

Three types of samples were used: as-received QCM monitors with sputter-coated metal electrodes (iron); solution-processed graphene drop-casted on the metal electrode; and Chemical Vapor Deposition (CVD)-grown graphene transferred on the metal electrode from the copper foil.

In case of solution-processed graphene, 1 mg/L graphene in ethanol solution purchased from Graphene Supermarkets was drop-casted on the top electrode, after which ethanol was evaporated for 1 h in dry nitrogen environment. The resulting coverage of the Solution Processed Graphene (SPG) was estimated to be around 50–60% of the total area (Supplementary Fig. 1) [22,30].

Single-layer graphene film was grown initially using a standard CVD procedure on the copper foil and transferred with poly(methyl methacrylate) PMMA layer onto metal electrodes to provide continuous coverage of the film [21]. Extra precautions were taken when rinsing graphene in DI water to eliminate any residue of the copper etchant, and thus to prevent its effect on the subsequent metal degradation. After transfer, additional PMMA layer was spin-coated on top of the sample to release the stresses in graphene film and all the polymer was removed by rinsing in acetone [31].

Supplementary Fig. 1 summarizes the images of CVD graphene and SPG graphene deposited on the samples. In case of solution processed graphene only partial coverage of graphene on the metal surface is observed. In case of CVD graphene, single layer film is transferred onto the whole surface of the electrode, and only occasional tears in the graphene film are observed.

### 2.2. QCM-based corrosion experiments

1-inch-in-diameter AT-cut Quartz Crystal Monitors with iron-coated electrodes were purchased from Fill-Tech Solutions, Inc. The fundamental resonant frequency of the monitors is on the order of 5 MHz. The measurements were performed using SRS QCM 200 analyzer. The specifically designed holder allows contact of the QCM with the liquid only at one side, while the second electrode and electric connections are isolated from the water environment to prevent corrosion of the contacts. When the samples were immersed in a liquid environment, resonant frequency and resistance were monitored after an initial 60 s equilibration period.

As a corrosion-inhibiting environment, 3 wt% of NaCl solution in DI water was prepared. The QCM samples were placed initially in the pure DI water to monitor the effect of the viscous environment on the mechanical resistance of sliding. After drying, the samples were placed in a corrosive NaCl solution and the change in frequency and mechanical resistance of oscillations were monitored. In all the tests, the amount of a sodium chloride solution is large, and periodic stirring of the liquid is performed to reduce the concentration of the dissolved material near the QCM surface and thus to neglect the effect of metal degradation on the density and viscosity of the surrounding medium. The tests were performed under corrosive environment for minimum of 1.5 h.

### 2.3. Characterization techniques

Scanning Electron Microscopy (SEM) images with Energy Dispersive Spectra (EDS) analysis were collected with FEI NOVA 200 system. Optical images of the samples after corrosion were collected using Zeiss Axiocam 506 Optical Microscope. Raman spectra of the resulting films were collected using Nicolet Almega XR Dispersive Raman spectrometer with green light laser ( $\lambda = 532$  nm). 2D Raman mapping of the samples was performed with 1  $\mu\text{m}$  step resolution. X-ray Diffraction (XRD) images for iron surface before and after corrosion is collected with Rigaku Ultima III Diffractometer with Copper K-alpha radiation ( $\lambda = 0.154$  nm).

Electrochemical potential mapping of the CVD graphene coated iron QCM was monitored in 3 wt% of NaCl solution in DI water using Kelvin Probe Mode in VersaScan Scanning Electrochemical Microscope (SECM). The freshly-prepared iron electrode sample was partially covered with transferred CVD-grown single-layer graphene. The sample was glued into the epoxy mold to insulate the electrode backside contact pads. The whole system was immersed into 3 wt% NaCl solution, and the evolution of the electrochemical potential on the sample surface was monitored at 1-h time intervals. Imaging was performed using platinum tip scanning above the surface with 0.1  $\mu\text{m}$  step.

## 3. Results

QCMs have been previously used for evaluating corrosion rates, but mostly based on the materials losses only [32,33]. Here, by monitoring simultaneously changes in the resonant frequency and mechanical resistance of QCM oscillations, we evaluated propagation of corrosion in graphene-protected samples. We performed comparative studies for three types of samples: QCM with uncoated bare metal electrode; QCM with CVD graphene transferred on the metal electrode (~90% coverage); and QCM with the metal electrode coated by graphene from ethanol solution (~50–60% coverage).

QCM resonators were placed in the sodium chloride solution (3 wt% NaCl in DI water), and the changes in resonant frequency and mechanical resistance of the oscillations as a function of time were recorded. Sodium chloride solution as a corrosive

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