Ultra-thin Graphene Coating: The Novel Nanotechnology for Remarkable Corrosion Resistance

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Graphene, an atomically thin film of a honeycomb network of sp^2 hybridized carbon atoms (shown in Figure 1 (*left*) [1]) has triggered unprecedented research excitement for its exceptional characteristics. What is most relevant for this presentation is the remarkable chemical inertness of graphene (even to the most aggressive chemicals such as HF) as well as its impermeability for fluids and gases [2]. The primary requirements of an ideal surface barrier coating for corrosion resistance are its: (a) inherent resistance/immunity to degradation in aggressive environment, (b) effective resistance to permeation of corrosive fluid, and (c) mechanical integrity over the desired life of the coated components. Ceramics and carbon-based engineering materials (such as graphite) are well-known to be immune to most aggressive chemicals. However, because these materials are very brittle, they suffer mechanical disruptions, and hence, have found limited use as coating. In contrast, atomically thin layer of graphene is reported to possess very high toughness. With its attributes of chemical inertness, toughness and impermeability, the ultra-thin graphene films possess a great potential as the durable corrosion resistant coating [3]. Studies hitherto, on the use of graphene as corrosion resistant coating [3-7], and they are all extremely recent.

Coatings of monolayer or a few atomic layer thick graphene sheet (Figure *(left)*) [1] have been shown to improve corrosion resistance on copper, by up to two orders of magnitude (Figure *(right)*). Though there are very few studies reported on the topic of corrosion resistance due to graphene coating, there is still considerable variability in the degree of improvement. For example, improvement in aqueous corrosion resistance of copper due to graphene coating is reported to vary from insignificant to 2 orders of magnitude [6], whereas the improvement for nickel can be in excess of an order of magnitude. This presentation will review the most recent research on graphene that has been claimed as 'the thinnest known corrosion-protecting coating', and examine the potential application of such disruptive approach to corrosion resistance of common engineering alloys such as mild steels. The presentation will also include the most recent work in the authors' group to show the durable corrosion resistance due to graphene coating.

Corrosion of engineering alloys is a vexing problem and traditional approaches (such as by suitable alloying or traditional coatings) have brought about significant but only incremental mitigation. In contrast, just an ultra-thin (a couple of atomic layers) of graphene on metals has been found to bring about disruptive improvements in corrosion resistance [3-6]. Little is reported on the corrosion resistance due to such ultrathin graphene coatings on the most common engineering alloys such as steels. Corrosion of such alloys and its mitigation measures cost any developed economy ~4% of their GDP (*i.e.*, ~\$8b annually to Australia and ~\$250b to USA). Thus, a durable corrosion mitigation of such alloys due to the disruptive approach of graphene coating is immensely attractive. This presentation will also describe the challenges and opportunities in this respect.

References:

1. AK Geim, KS Novoselov, The rise of graphene, *Nature Materials*, 6 (2007) 183.

2. E Stolyarova, D Stolyarov, K Bolotin, S Ryu, L Liu, KT Rim et al. Observation of graphene bubbles and effective mass transport under graphene films. *Nano Letters,* 9 (2012) 332.

3. D Prasai, J Tuberquia, RR Harl, GK Jennings, KI Bolotin, Graphene: Corrosion-Inhibiting Coating, **ACS Nano,** 6 (2012) 1102.

4. S Chen, L Brown, M Levendorf, W Cai, S-Y Ju, J Edgeworth, X Li, CW Magnuson, A Velamakanni, RD Piner, J Kang, J Park, RS Ruoff, Oxidation Resistance of Graphene-Coated Cu and Cu/Ni Alloy, *ACS Nano*, 5 (2011) 1321.

5. N Kirkland, T Schiller, N Medhekar, N Birbilis, Exploring graphene as a corrosion protection barrier, *Corros Sci*, 56 (2012) 1.

6. ŘK Singh Raman, PC Banerjee, DE Lobo, H Gullapalli, M Sumandasa, A Kumar, L Choudhary, R Tkacz, PM Ajayan, M Majumder, Protecting Copper from Electrochemical Degradation by Graphene Coating, *Carbon*, 50 (2012) 4040.

7. Schriver M, Regan W, Gannett WJ, Zaniewski AM, Crommie MF, Zetti A, Graphene as a Long-Term Metal Oxidation Barrier: Worse Than Nothing, ACS Nano, 2013, 10.1021/nn4014356.

