

# Towards the suppression of biocorrosion and biofouling through graphene coatings.

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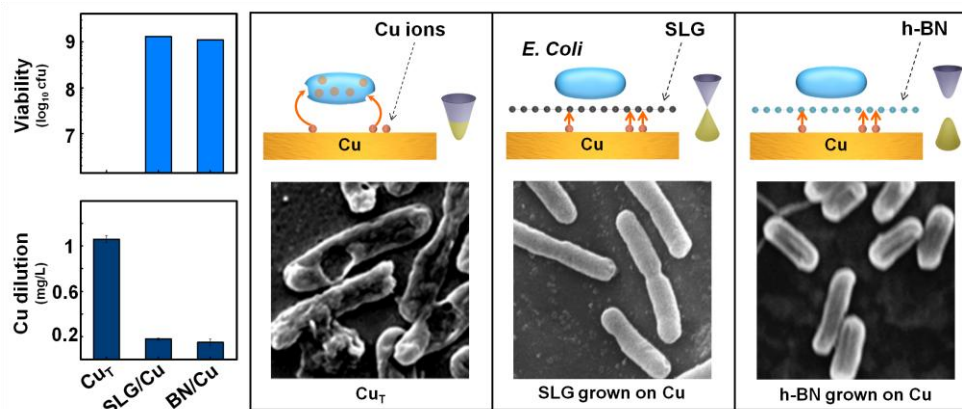
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Biocorrosion of man-made materials occurs when microorganisms in different environments interact strongly with them, creating a highly accelerated corrosion. This phenomenon reports costs hundreds of millions of dollars a year in maintenance and repair of damaged infrastructure in sectors such as metallurgy and construction [1, 2], and is also relevant in the field of medical implants [3]. In the case of the mining industry, water from natural streams used for industrial processes possesses various microorganisms that produce bio-corrosion damage in pipelines of water transportation systems. Current strategies to control biocorrosion mainly comprise applying epoxy coatings, which have only temporary protection.

Another important phenomena involving the colonization of artificial and natural surfaces by unwanted microorganisms is known as biofouling, and has an important economic impact on a wide range of industries as well [4]. Current antifouling strategies are typically based on biocides which exhibit a negative environmental impact, affecting surrounding ecosystem [4].

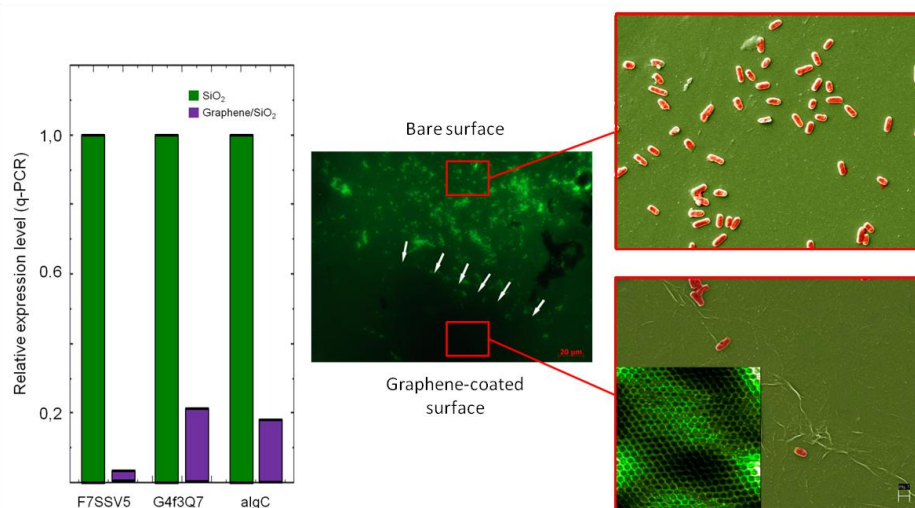


**Figure 1:** Summary of results for interaction between bacteria and graphene-coated copper interaction inferred from our study. (left) Viability, Atomic Absorption Spectroscopy(AAS) results confirmed graphene and h-BN coatings prevent interaction between underlying metal and bacteria. (right) Metal do not see bacteria (do not suffer biocorrosion) and bacteria do not feel metal (do not feel bactericide activity of metals) as confirmed by SEM images and AAS [5].

Considering critical processes resulting in biocorrosion and biofouling occur in the nanoscale/microscale dimensions, in this work we present a microbiological and bionanotechnological approach to reduce metal biocorrosion and adhesion of biofouling-producing bacteria by introducing graphene coatings. For the biocorrosion point of view our results demonstrate that such graphitic coatings substantially suppress interaction between

bacteria and underlying metallic substrates (Cu and Ni), acting as an effective barrier to prevent physical contact [5]. Bacteria do not “feel” the strong bactericide effect of Cu or Ni, and the metallic substrate does not suffer biocorrosion due to bacteria contact (See Figure 1). Effectiveness of these systems as barriers can be understood in terms of graphene impermeability to transfer  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions, even when graphene domain boundary defects are present. In the case of graphene-coated Ni foils, we observed absence of  $\text{Ni}^{2+}$  ions release, even when in contact with artificial sweat, indicating a potential application of graphene coatings to reduce hypersensitivity to Ni, the most frequent contact allergy to man-made products [6]. In the case of biofouling, our study revealed that graphene coatings modify surface energy and electrostatic interactions with bacteria which determines an important reduction over resulting bacterial adhesion (Figure 2) [7]. This nanoscale surface modification affects the expression levels of genes related to adhesion that are notoriously reduced when bacteria are in contact with graphene-coated material. Our results demonstrate that graphene coatings reduce considerably adhesion of biofouling-producing bacteria. In addition no bactericide effect of graphene coatings was observed. The effect over biofilm formation is localized right at coated surface, in contrast to current antifouling techniques, such as biocides.

Our results seem to indicate that as-grown graphene films could successfully prevent biofouling and biocorrosion for biological, industrial and medical applications [8].



**Figure 2:** (left) Relative expression levels of 3 adhesin genes for biofouling-producing bacteria in contact to graphene-coated and uncoated SiO<sub>2</sub>. (right) Epifluorescence and SEM measurements confirm reduction of bacterial adhesion to graphene-coated surfaces.(inset) STM image of graphene transferred onto SiO<sub>2</sub>.

## References

- [1] C.W. Keevil, Water Science and Technology Vol 49 No 2 (2010) 91–98.
- [2] K. Li et al. Corrosion Reviews 31 (2013) 73-84.
- [3] D.C.Hansen, Electrochem. Soc. Interface, Summer 31, 2008.
- [4] Tuson HH, Weibel DB. Bacteria-surface interactions. Soft Matter 9 (2013) 4368- 4380.
- [5] C. Parra, F. Montero-Silva et al., ACS Appl. Mater. Interfaces 7(12), 6430 (2015).
- [6] Ben Roediger and Wolfgang Weninger, Immunology and Cell Biology 89 (2011) 1–2.
- [7] C. Parra, F. Dorta et al., Submitted to Journal of Nanobiotechnology (2015).
- [8] This work was financially supported by Conicyt de Inserción #791220009 and #791100037, Fondecyt grant #1110935 and #1110992, Proyecto Interno DGIP #111469 and #111470, PIA anillo ACT 1117, Mecesup FSM1204 and Innova Corfo L1 13IDL1-25496.