

# Graphene ink as a corrosion inhibiting blanket for Iron in aggressive chloride environment

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## Supplementary information

### 1. Experimental:

#### Synthesis of Graphite oxide.

Graphene oxide (GO) was obtained by the modified Hummers method.<sup>[1]</sup> 2 g of graphite powder (SP1, Bay carbon), 2 g of sodium nitrate, and 96 mL of conc. H<sub>2</sub>SO<sub>4</sub> were mixed together at 0 °C. 12 g of KMnO<sub>4</sub> was gradually added to the above mixture and stirred for 90 min at 0 °C and then at 35 °C for 2 h. 80 mL of distilled water was slowly added into the resulting solution. Then 200 mL of distilled water was added followed by 10 mL of H<sub>2</sub>O<sub>2</sub> (30%), to obtain a graphite oxide suspension. The graphite oxide deposit was collected from the graphite oxide suspension by high-speed centrifugation at 10000 rpm for 10 min, and repeatedly centrifuged and washed with distilled water until pH 7 is reached. The wet graphite oxide was dewatered by vacuum drying at 90° C for 12 h.

#### Synthesis of Graphene Ink

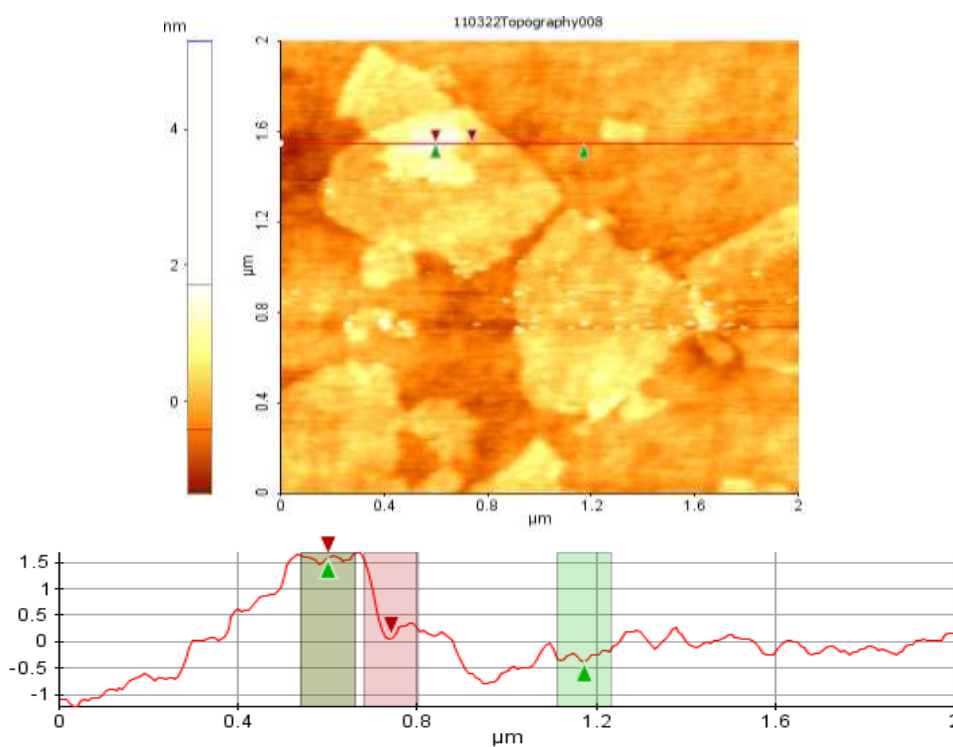
Graphene Ink was prepared by adding 0.05g of as-prepared GO powder to a 10 ml aqueous solution of 0.5 wt% poly (sodium styrene sulfonated) PSS. The mixture was sonicated for 10 minutes to exfoliate the graphite oxide to obtain a GO/PSS aqueous suspension. Finally, the GO/PSS suspension was reduced with sodium borohydride (Sigma Aldrich) to form reduced graphene oxide sheet stabilized by PSS.

A known amount of Graphene Ink (or PSS solution) was spin/drop casted onto Fe surface and dried at 80°C to form Graphene Ink coated (or PSS coated) Fe surface.

#### Instrumentation

Raman spectra were recorded using a high resolution dispersive Raman microscope employing a He-Ne laser of 1 mW at 633 nm. X-ray diffraction (XRD) patterns of the samples were measured using Bruker X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) measurement was performed with Sigma probe X-Ray Photoelectron Spectrometer (Thermo VG Scientific) with Al K $\alpha$  X-ray for excitation. Surface morphology of the samples was measured by using a TESCAN scanning electron microscope. Energy-dispersive X-ray (EDX) analysis was obtained with an EDX detector installed on the same SEM. FT-IR spectra was recorded using Nicolet 380 FTIR instrument having ATR attachment (Thermo USA). AFM image was taken in tapping mode by using a VEECO AFM instrument (Digital

Instruments). EIS measurements were carried out on PAR STAT 2273 Impedance analyzer (Princeton Applied Research) using a conventional three-electrode cell with a platinum counter electrode and SCE (saturated calomel electrode) reference electrode. The working electrode for EIS experiment was prepared by thin film electrode method. A polished mild steel sample ( $2 \text{ cm}^2$ ) was used as a substrate. A  $40 \mu\text{l}$  aqueous solution of as-prepared Graphene Ink was spin/drop coated onto mild steel substrate and dried at  $80 \text{ }^\circ\text{C}$  to form a Graphene Ink coated working electrode. The PSS coated working electrode is prepared in the same way without Graphene.



**Figure S1: AFM image of GO sheets used in this work.**

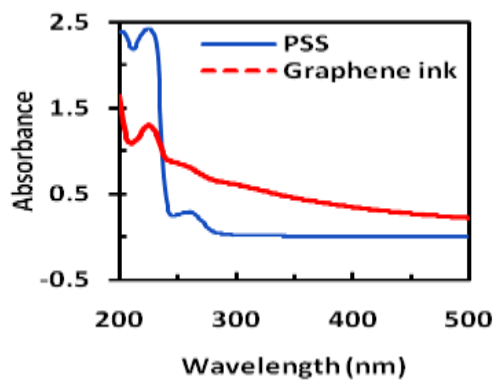


Figure S2: UV-vis spectra of PSS and Graphene Ink

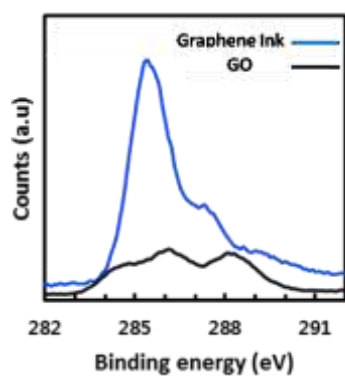


Figure S3. High resolution C 1s spectra of GO and Graphene Ink

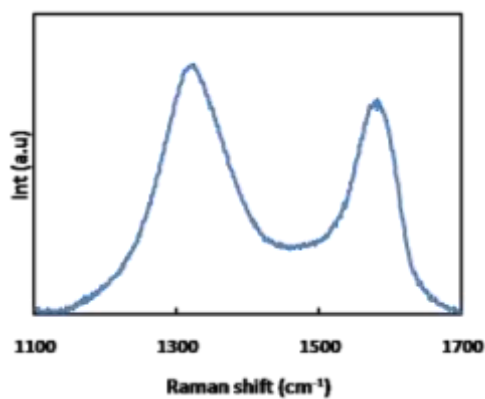
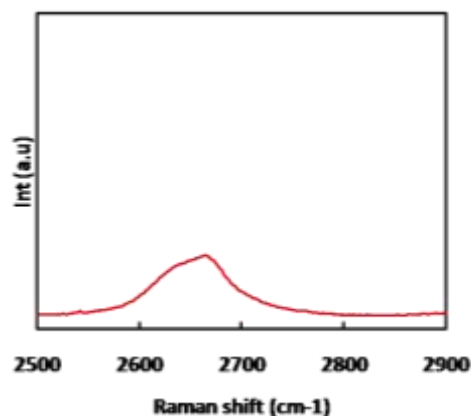
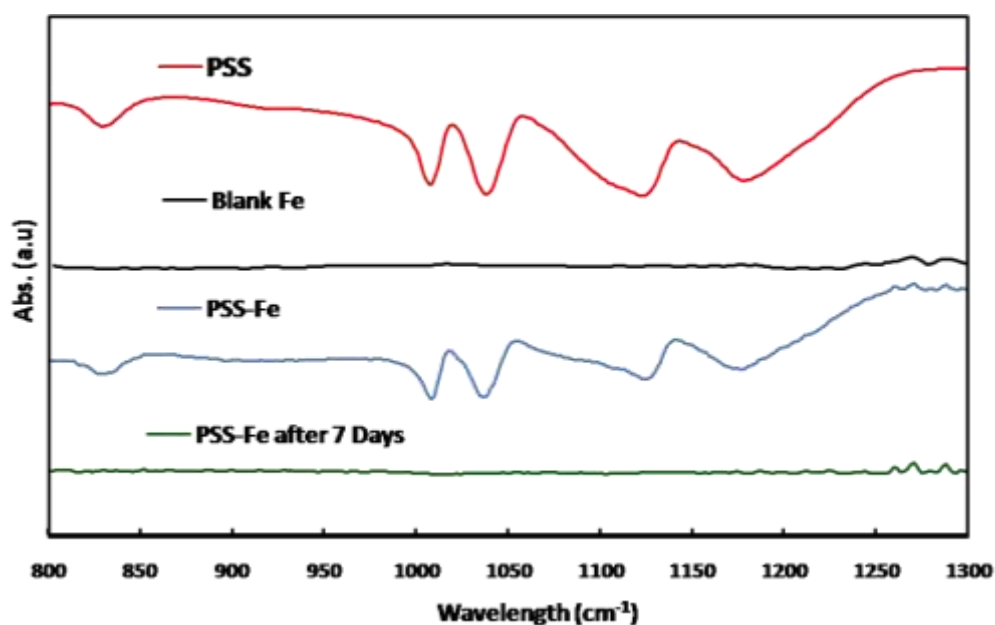


Figure S4: Raman spectra of as-prepared GO

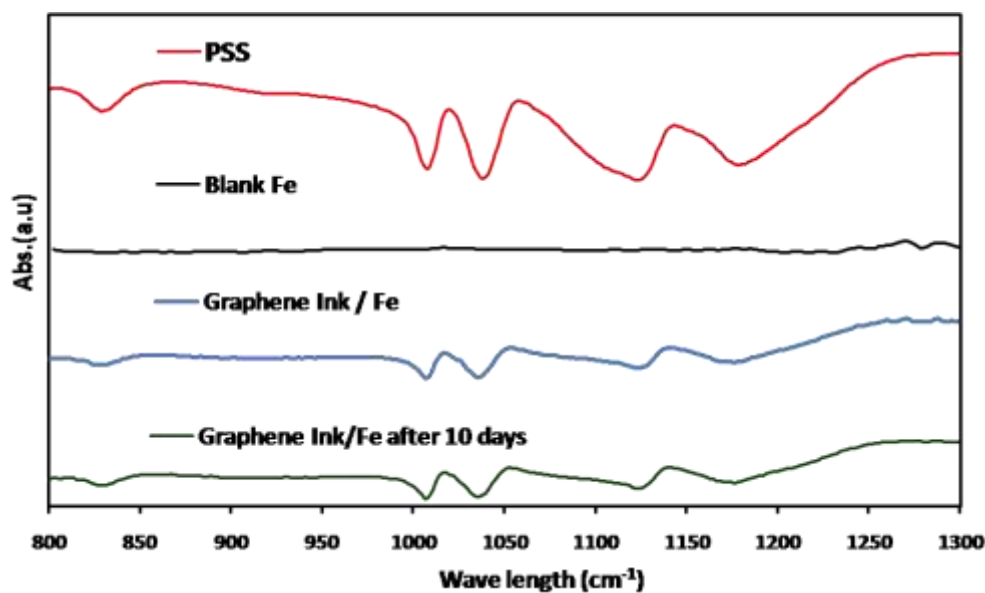


**Figure S5. 2D Raman spectra of Graphene Ink**

Raman spectra of Graphene Ink provide evidence for the existence of few layer graphene. The 2D peak is the most prominent feature of graphene in the Raman spectrum, and its position and shape can be used to clearly distinguish between single-layer, bilayer, and few-layer graphenes. For as-prepared Graphene Ink, the 2D peaks appear at around  $2700\text{ cm}^{-1}$ . Compared with the spectrum of single-layer graphene,<sup>[2]</sup> the as-prepared sample exhibit a broader and up-shifted peak in the Raman spectra, demonstrating that the reduction process in presence of PSS results in few-layer graphene sheets.



**Figure S6 (a) FTIR spectra of PSS, PSS/Fe**



**Figure S6 (b) FTIR spectra of PSS, Graphene Ink/Fe**

### **S7: Electrochemical Impedance Spectroscopy (EIS) evaluation of PSS/Fe and Graphene Ink/Fe**

Mild steel panel with the size of 2 cm × 2 cm × 0.2 cm coated with PSS and Graphene Ink was used in this study. Electrochemical impedance spectroscopy measurements were performed using the three electrode corrosion cell using Electrochemical Impedance Analyzer (PAR, 2273). Impedance measurements were carried out using Powersine software for a frequency range of 100 kHz to 0.1 Hz with an AC signal of rms amplitude of 20 mV for different exposure time in 1% NaCl. The measurements were with triplicate samples and the measured impedance values are reproducible to ± 2 to 3 %. From the impedance plots, the coating resistance ( $R_c$ ) and the coating capacitance ( $C_c$ ) values were calculated using Zsimpwin 3.21 software using the equivalent circuit for impedance data with one time constant as shown in Fig.S5a where  $R_s$  is the solution resistance,  $R_c$  is the coating resistance and  $Q$  is the constant phase element of the coating capacitance.

For the description of a frequency independent phase shift between an applied AC potential and its current response, a constant phase element (CPE) is used which is defined in impedance representation as

$$Z(Q) = Y_0^{-1} (j\omega)^{-n}$$

where  $Y_0$  is the CPE constant,  $\omega$  is the angular frequency (in  $\text{rad s}^{-1}$ ),  $j^2 = -1$  is the imaginary number and  $n$  is the CPE exponent ( $n > 0$ , for ideal capacitance  $Z(\text{CPE}) = C$ ,  $n = 1$ ). The following equation is used to convert  $Y_0$  into  $C_c$ ,

$$C_c = Y_0 \left( \omega_m \right)^{n-1}$$

where  $C_c$  is the coating capacitance and  $\omega_m$  is the angular frequency corresponding to a measurement at which  $Z''$  is maximum.

The impedance data with two time constants were analyzed using the equivalent circuit (Fig.S5b) where  $C_{dl}$  is the double layer capacitance and  $R_{ct}$  is the charge transfer resistance.

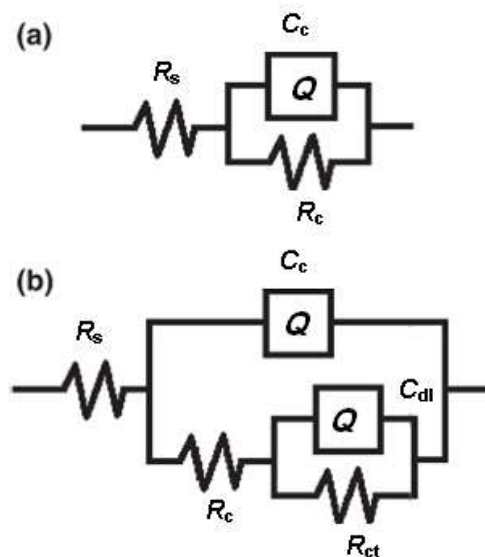


Figure S7: Equivalent circuit

## References

1. W. Lv, D. M. Tang, Y. B. He, C. H. You, Z. Q. Shi, X. C. Chen, C. M. Chen, P. X. Hou, C. Liu and Q. H. Yang, *ACS Nano*, 2009, **3**, 3730
2. C. H. Lui, L. Liu, M. F. Mak, G. W. Flynn, T. F. Heinz, *Nature*, 2009, 462, 339.