

Dynamic Mesoscale Interfacial Characterisation of Graphene and Graphene Oxide Thin Films in Water, Dodecane and their Vapour using QCM

R. Mazzocco*, B. J. Robinson*, J. Dickinson**, C. Boxall** and O. V. Kolosov*

*Department of Physics, Lancaster University, Lancaster LA1 4YB, UK

**Department of Engineering, Lancaster University, Lancaster LA1 4YB, UK

Corresponding author: r.mazzocco@lancaster.ac.uk

ABSTRACT

In this paper, we report the experimental work conducted on graphene and graphene oxide thin film coated Quartz Crystal Microbalance (QCM) exposed to DI water and dodecane, as well as corresponding water and dodecane close to saturation vapour, in the temperature range 20-60° C. Changes in interfacial properties are investigated by real-time measurements of QCM resonant frequency shift as well as motional resistance variation. We observed nanobubble adsorption/desorption on the graphene surface, graphene nano-flakes rearrangements as well as gas and liquid adsorption by the graphene layers when the graphene film was exposed to liquid and vapour phases. In liquid environment, increased temperature has induced consistent trends for the liquid mass uptake by the graphene and graphene oxide films.

Keywords: graphene, environments, liquids, gases, quartz crystal microbalance

1 INTRODUCTION

Graphene is a flat monolayer of carbon atoms arranged in a honeycomb structure whose extraordinary properties have generated a lot of excitement in the scientific community [1]. Its reported high surface-to-mass ratio, large electrical conductivity and electron mobility as well as its outstanding optical and mechanical properties, make it suitable for a wide variety of applications spanning from energy storage devices to transistors and displays [2]. Since it was first isolated in 2004, graphene has been object of extensive study in vacuum and dry environment, but very little work has been carried out on graphene in less ideal environments such as liquids and gases [3]. Examples of studies in liquid environments encompass some preliminary theoretical simulations [4, 5] as well as little experimental work [3, 6, 7] mostly aimed to target very specific aspects such as the exploitation of its hydrophobicity in the development of water-repellent coatings and its potential employment in sensor technologies. However, what can be found in literature is clearly insufficient to provide thorough understanding of how the properties of graphene are affected by its working environment; in particular, the compatibility between graphene and polar/non-polar liquids remain poorly understood, despite being crucial for energy

storage applications such as supercapacitors and batteries [8]. This paper is to our knowledge, the first exploration of such phenomena in graphene films using highly sensitive to interfacial phenomena QCM method that can broaden the understanding of graphene/liquid interfacial physical processes.

QCM is a very high sensitive instrumental technique that allows the study of physical interfaces by probing electrode-mass changes down to the nanogram [9]. Typically, QCM comprises a thin AT-cut quartz crystal sandwiched between two metal electrodes that induce vibrational motion of the crystal by establishing an alternating electric field across it. Such vibration occurs at the resonant frequency of the crystal that mainly depends on its thickness. Any detectable addition of mass on the electrode determines a frequency drop which extent is proportional to the added mass according to the Sauerbrey equation [10].

$$\Delta f = -2f_0^2 \frac{\Delta m}{A\sqrt{\mu_q \rho_q}} \quad (1)$$

QCM not only provides information concerning mass changes but also crystal conductance, which links interfacial motional variations to major parameters such as the viscosity of the medium and toughness at the electrode/medium interface as well as the elasticity of the thin film being examined [11].

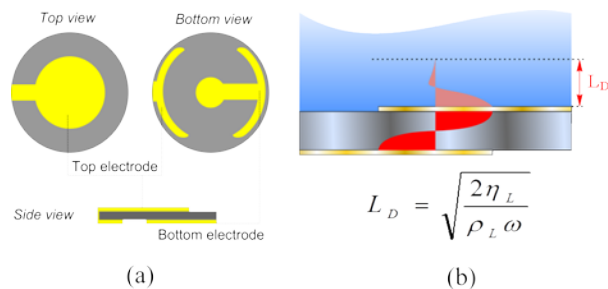


Figure 1: (a) QCM with the top and bottom electrode (b) shear wave decay length depends on the viscosity and density of the liquid medium.

In this work, a set of quartz crystals coated with graphene and graphene oxide thin films were exposed to water and dodecane, both in the liquid and gas phases, in order to study mesoscale changes in the physical properties

of these films in the presence of polar and non-polar liquids and corresponding gases.

2 EXPERIMENTAL DETAILS

2.1 Sample preparation

Several methods for graphene oxide (GO) production may be found in the literature, predominantly employing means of strong oxidising and potentially explosive mixtures to oxidise graphite thus forming GO [12]. A safer method was developed by Hummers [13] and further refined by Becerril [14], who produced GO using an oxidising mixture of concentrated sulphuric acid and potassium permanganate to treat graphite powder, which is the method used in this study and the favoured method in literature.

The GO used in this study was fabricated using a refined Hummers method described by Becerril [14]. Crystals were thoroughly cleaned and spin-coated in GO solutions; these samples were denominated GO. Two of the above samples were thermally reduced in order to produce graphene samples denominated G. Thermal reduction was performed by placing them into a nitrogen filled furnace.

2.2 QCM experimental setup

The full QCM experimental setup consisted of a phase locked oscillator (Maxtek PLO 10i) providing the resonant frequency and a dc voltage proportional to the crystal's conductance, a frequency counter to measure frequency shifts (HP 53131A) and a multimeter (Keithley 6430) to measure the dc signal mentioned above. Both instruments were connected to a PC via a GPIB-USB interface so as to acquire data in real time by means of a LabVIEW™ based virtual instrument specifically developed for this experiment (see Figure 2).

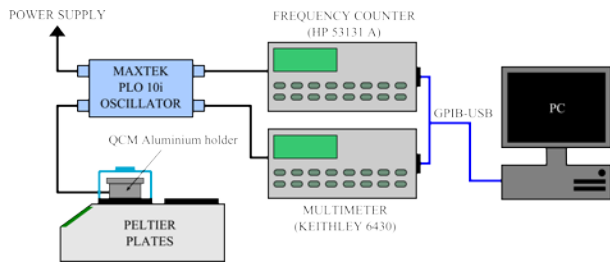


Figure 2: Schematic of experimental setup

Two liquids have been investigated, deionised water (DI) (H_2O) and dodecane ($C_{12}H_{26}$). The main reason for this choice is the substantial difference in polarity between water and dodecane; in fact, water bonds are polar covalent (electronegativity 1.24) while dodecane bonds are non-polar covalent (electronegativity 0.35). These compounds lie at two extremes of the polarity scale, while any other

electrolyte used in industry should fall within the polarity range confined by these two liquids.

An aluminium holder insulated with rubber rings was developed to house the crystals; the holder's lid incorporated a threaded bore to inject liquids by means of a syringe. In order to control the temperature within the established range, a double Peltier plate was employed; setting the two plates at different temperatures allowed rapid change between temperature steps, to the crystal holder, by avoiding waiting for the Peltier heater to heat up a single plate. Two different sets of experimental studies were conducted, with de-ionised (DI) water and dodecane in the liquid phase (underliquid measurements) and in the close to saturation but non-condensing vapour environments of these liquids.

3 RESULTS AND DISCUSSION

3.1 Underliquid measurements

A crystal was arranged in the aluminium holder and was held firm by means of two o-rings pressed down by an aluminium lid featuring a threaded bore and a screw, suitable for injecting liquid with a syringe once temperature has stabilised at the desired value. We measured the baseline change in frequency with temperature for the uncoated crystals this was approximately linear with a drop of 47.4 Hz per $10^\circ C$. This baseline frequency shift was taken into account in the graphene sample measurements. The changes in losses (QCM conductance) with T were found to be negligible. The experiment consisted of three steps; in the first one the aluminium setup containing a dry crystal was placed on a Peltier plate set at $20^\circ C$ and frequency and losses values were recorded every 2 seconds. The second step began as soon as frequency had settled at a reasonably constant value, being its maximum variation within 1-2% of the average. Liquid was injected through the threaded aperture to entirely cover the coated surface; once the whole setup was stable in temperature ($20^\circ C$), the last step could begin. In this third step the temperature was raised up to $60^\circ C$ while the frequency and losses trends continued to be recorded every 2 seconds as in the first two steps. The experiment ended when there were no more significant variations in frequency and/or losses.

What clearly arose from underliquid measurements is that for both graphene and graphene oxide there was an evident frequency rise after the temperature was increased to $60^\circ C$, suggesting a mass decrease occurring in the graphene layers. Such a rising trend was found to be consistent both in water and dodecane, albeit exhibiting different timescales and behaviour in the long run. While in water this apparent mass decrease lasted for approximately an hour and a half (~ 83 min) in dodecane it showed no signs of change after over two hours. Moreover, an increase in crystal resistance manifested itself in a fairly similar

fashion, indicating a corresponding dissipation rise at graphene-liquid interface.

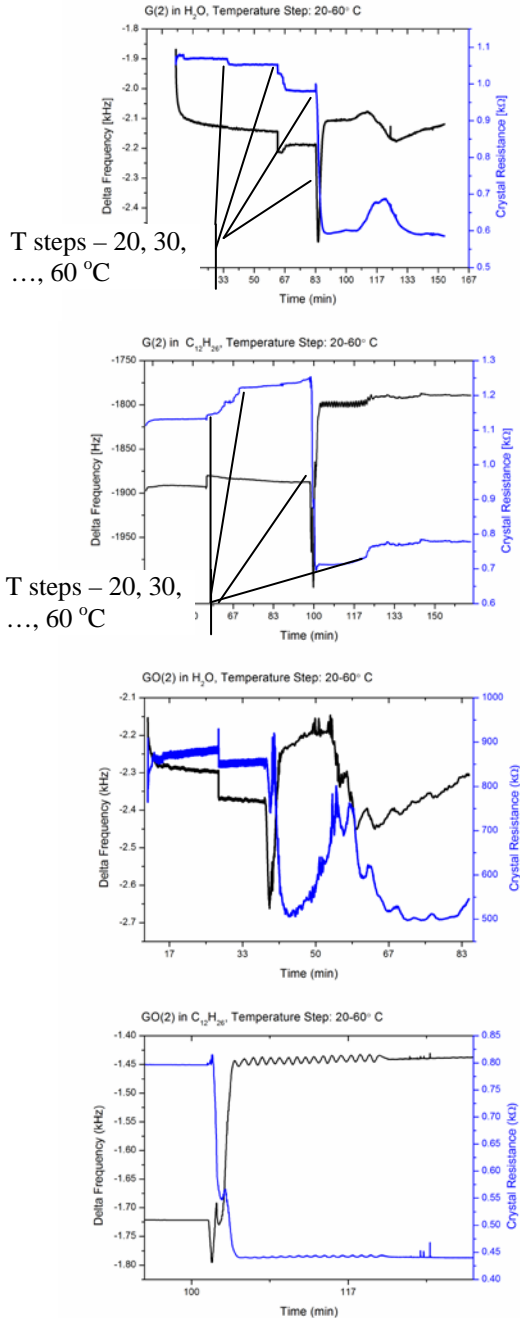


Figure 3: Graphene (G(2)) and graphene oxide (GO(2)) coated quartz crystals in water (H₂O) and dodecane (C₁₂H₂₆) when a 40° C temperature step is applied.

The reason for such mass decrease may be leaching of contaminants from graphene but also a formation of bubbles on solid-liquid interface. A number of papers on QCM have reported the formation of such nanobubbles at solid-liquid interfaces [10, 15, 16]; with their nucleation happening typically in a matter of seconds, up to a minute,

whereas their lifetime can be much longer [16]. The gaseous nature of this interfacial state has been confirmed by QCM studies. However, solid understanding of their properties and nucleation process remain elusive.

Also we believe losses in graphene-to-graphene flake adhesion at elevated temperatures may also lead to changes in observed mass and dissipation. Further work is certainly needed in order to refine the outcome as well as gaining a deeper understanding of such phenomena.

3.2 Gaseous measurements

In this experiment, temperature was kept constant at 60° C for water and 80° C for dodecane (compensating for lower vapour pressure of dodecane). The measuring process comprises only two steps in this case, though the second one was repeated twice or more to assess the consistency of the trend. The first step, as in the underliquid measurements, was the stabilisation in temperature of the dry crystal, while in the second step, a disc of filter paper arranged into the aluminium setup was sprinkled with some water/dodecane (approximately 500 µl) to study how the subsequent evaporation of liquid molecules would have affected the coated surface of the crystal.

Liquids were supplied by sprinkling a filter paper disc arranged inside the QCM holder with a syringe. With water, soon after a dramatic frequency drop, evaporation exhibiting exponential-like behaviour was noted in two distinct time regions. In these regions, the exponential trend featured diverse time constants as if two overlapping phenomena were taking place in sequence. The liquid injection was performed twice to observe potential differences in the process development, however the exponential trend looked consistent in every instance both for graphene and graphene oxide coated crystals. In the case of dodecane a similar phenomenon seemed to take place, although the time constant of each step was different.

We attribute these changes in “drying regime” to the initial evaporation of thin liquid film attached to the surface followed by the subsequent evaporation of the residual liquid contained between the graphene flakes. It is interesting to note that apparently more water than dodecane is retained in the layer of graphene, as well as to drying GO from water happens simultaneously with drying the liquid film.

4 CONCLUSIONS

In summary, we developed a new methodology for studying graphene – liquid interactions of thin layers of graphene and graphene oxide. We were able to explore changes in swelling of graphene and GO layers in polar (water) and non-polar (dodecane) liquids and demonstrated a complex multistage behavior of absorption of water vapour in graphene film.

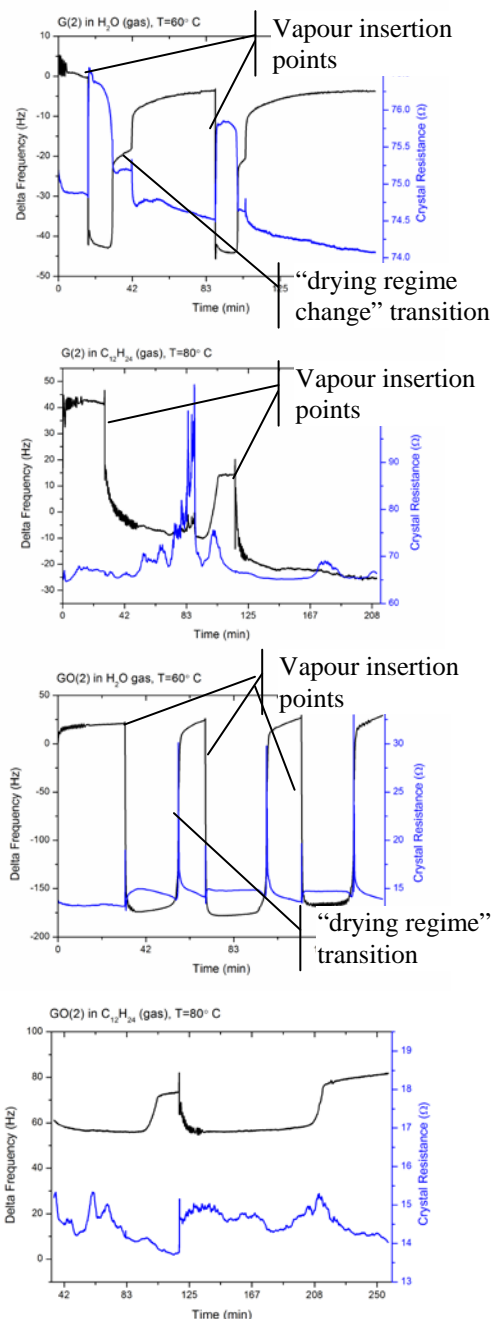


Figure 4: Graphene (G(2)) and graphene oxide (GO(2)) coated quartz crystals in gases (H_2O at 60°C and $\text{C}_{12}\text{H}_{26}$ at 80°C).

REFERENCES

1. Novoselov, K.S., et al., *Electric field effect in atomically thin carbon films*. Science, 2004. **306**(5696): p. 666-669.
2. Brownson, D.A.C., D.K. Kampouris, and C.E. Banks, *An overview of graphene in energy*

- production and storage applications. Journal of Power Sources, 2011. **196**(11): p. 4873-4885.
3. Rafiee, J., et al., *Wetting transparency of graphene*. Nat Mater, 2012. **11**(3): p. 217-222.
4. Wehling, T.O., A.I. Lichtenstein, and M.I. Katsnelson, *First-principles studies of water adsorption on graphene: The role of the substrate*. Applied Physics Letters, 2008. **93**(20).
5. Cole, D.J., P.K. Ang, and K.P. Loh, *Ion Adsorption at the Graphene/Electrolyte Interface*. The Journal of Physical Chemistry Letters, 2011. **2**(14): p. 1799-1803.
6. Hsieh, C.-T. and W.-Y. Chen, *Water/oil repellency and work of adhesion of liquid droplets on graphene oxide and graphene surfaces*. Surface and Coatings Technology, 2011. **205**(19): p. 4554-4561.
7. Yavari, F., et al., *Tunable Bandgap in Graphene by the Controlled Adsorption of Water Molecules*. Small, 2010. **6**(22): p. 2535-2538.
8. Liu, C., et al., *Graphene-Based Supercapacitor with an Ultrahigh Energy Density*. Nano Letters, 2010. **10**(12): p. 4863-4868.
9. Yao, Y., et al., *Graphene oxide thin film coated quartz crystal microbalance for humidity detection*. Applied Surface Science, 2011. **257**(17): p. 7778-7782.
10. Buttry, D.A. and M.D. Ward, *MEASUREMENT OF INTERFACIAL PROCESSES AT ELECTRODE SURFACES WITH THE ELECTROCHEMICAL QUARTZ CRYSTAL MICROBALANCE*. Chemical Reviews, 1992. **92**(6): p. 1355-1379.
11. Martin, S.J., et al., *Resonator oscillator response to liquid loading*. Analytical Chemistry, 1997. **69**(11): p. 2050-2054.
12. Brodie, B.C., *On the Atomic Weight of Graphite*. Philosophical Transactions of the Royal Society of London, 1859. **149**(ArticleType: research-article / Full publication date: 1859 /): p. 249-259.
13. Hummers, W.S. and R.E. Offeman, *PREPARATION OF GRAPHITIC OXIDE*. Journal of the American Chemical Society, 1958. **80**(6): p. 1339-1339.
14. Becerril, H.A., et al., *Evaluation of solution-processed reduced graphene oxide films as transparent conductors*. ACS Nano, 2008. **2**(3): p. 463-470.
15. Brotchie, A. and X.H. Zhang, *Response of interfacial nanobubbles to ultrasound irradiation*. Soft Matter, 2011. **7**(1): p. 265-269.
16. Zhang, X.H., *Quartz crystal microbalance study of the interfacial nanobubbles*. Physical Chemistry Chemical Physics, 2008. **10**(45): p. 6842-6848.