

# Control of Water Adsorption via Electrically Doped Graphene

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## Abstract:

The interaction of graphene with water molecules under an applied electric field is not thoroughly understood, yet this interaction is important to many thermal, fluidic, and electrical applications of graphene. In this work, the effect of electrical doping of graphene on water adsorption was studied through adsorption isotherms and current-voltage (IV) characterizations as a function of the Fermi level. The water adsorption onto graphene increased  $\sim 15\%$  and the doping levels increased by a factor of three with a gate-to-graphene voltage of +20 or -20V compared to 0V for sub-monolayer adsorption. This change in uptake is attributed to the increase in density of state of graphene upon electrical-doping, which changes the Coulombic and van der Waals interactions. The water adsorption onto graphene is either *n*- or *p*-doping depending on the applied gate-to-graphene voltage. The ambi-doping nature of water onto graphene is due to the polar nature of water molecules, so the doping depends on the orientation of the water molecules.

## Summary of Research:

Being extremely thin and thermally stable, graphene is an appealing method of surface modification [1-3]. It has been noted that water adsorption onto a supported graphene changes graphene's electronic structure. However, how water adsorption changes with altering the graphene Fermi level has never been studied experimentally [4].

We set out to test the hypothesis that the water adsorption behavior onto graphene can be tuned by electrically shifting the Fermi level, and hence the energetics of adsorption. In order to test this hypothesis, water adsorption onto back-gated graphene field effect transistors (GFETs) was studied as a function of electrical-doping via a quartz crystal microbalance (QCM) and current-voltage (IV) curve measurements.

Back-gate GFETs were fabricated onto 5 MHz AT-cut QCMs. An adhesion layer, 100 nm of Ti, was deposited onto the top electrode of the QCM via e-beam evaporation (AJA International). A 100 nm  $\text{Al}_2\text{O}_3$  was deposited via atomic layer deposition (ALD) with trimethylaluminum (TMA) and oxygen plasma at 200°C (Oxford Flex AL) to form the dielectric onto the QCM.

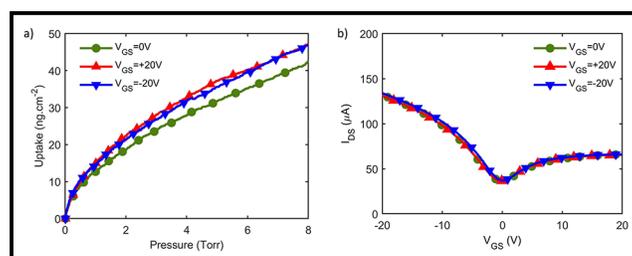


Figure 1: Adsorption isotherms were measured in an environmental vacuum chamber using the shift in the resonance frequency of the QCM upon water vapor exposure. (a) Shows the adsorption isotherms of water onto graphene for three different gate voltages: 0V, +20V, and -20V. (b) The three applied gate voltages during water adsorption induced no doping, n-doping, and p-doping, respectively.

Then, PMMA-backed CVD graphene was transferred onto the QCM. After the PMMA removal, the source and drain (5 nm Cr / 100 nm Au) were deposited on top of graphene via e-beam evaporation (AJA International), creating a 7.1 mm  $\times$  7.1 mm channel.

Adsorption isotherms were measured in an environmental vacuum chamber using the shift in the resonance frequency of the QCM upon water vapor exposure. Figure 1a shows the adsorption isotherms of water onto graphene for three different gate voltages: 0V, +20V, and -20V. The three applied gate voltages during water adsorption induced no doping, *n*-doping, and *p*-doping, respectively (Figure 1b). It can be seen in Figure 1a that the non-zero-gate voltages led to higher uptakes. However, switching the gate voltage polarity resulted in similar uptakes.

This change in uptake for the doped graphene is attributed to the change in the Coulombic and van der Waals interactions due to the increase in density of state (DOS) of graphene upon doping [5].

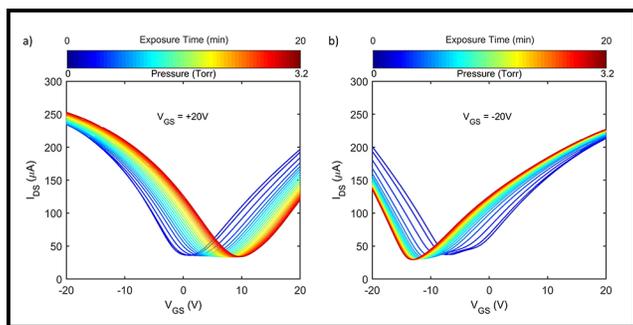


Figure 2: The IV curves after water vapor exposure with different applied gate voltages. (a) The adsorption of water molecules shifted the  $V_{CNP}$  in the positive direction and made the graphene less *n*-doped. (b) The adsorption of water molecules moved the  $V_{CNP}$  in the negative direction and made the graphene less *p*-doped.

In a different set of experiments, IV scans were periodically conducted after  $x$  minutes of water vapor exposure ( $x = 0, 1, 2, \dots, 20$ ). Figure 2 shows the IV curves after water vapor exposure with different applied gate voltages.

During the adsorption with an applied gate voltage of +20V, the graphene was initially *n*-doped; however, the adsorption of water molecules shifted the  $V_{CNP}$  in the positive direction and made the graphene less *n*-doped (Figure 2a), i.e., water adsorption induced holes in graphene. On the other hand, when the applied gate voltage was kept at -20V during adsorption, the graphene was initially *p*-doped; however, the adsorption of water molecules moved the  $V_{CNP}$  in the negative direction and made the graphene less *p*-doped (Figure 2b), i.e., water adsorption induced electrons in graphene.

When the applied gate voltage ( $V_{GS}$ ) is greater than the  $V_{CNP}$ , electrons are the dominant charge carriers in graphene, so that water molecules tend to adsorb onto graphene with the positive side of the dipole (the H atoms) towards graphene. This creates a dipole layer of water molecules with their positive charge next to the graphene that induces *p*-doping. Figure 2a supports this hypothesis, as when  $V_{GS} = +20V$  was greater than  $V_{CNP}$ , the  $V_{CNP}$  shifted in the positive direction, which indicates water is *p*-doping graphene.

Conversely, when the gate voltage is less than the  $V_{CNP}$ , the water molecules adsorb onto graphene with their negative charges toward the graphene (the OH bonds upward), which creates a dipole layer of water molecules and induces *n*-doping. This agrees with Figure 2b, where  $V_{GS} = -20V$  was less than  $V_{CNP}$ , and the  $V_{CNP}$  shifted in the negative direction, which indicates water is *n*-doping graphene (Figure 3).

A detailed discussion of this research can be found at Ref 4.

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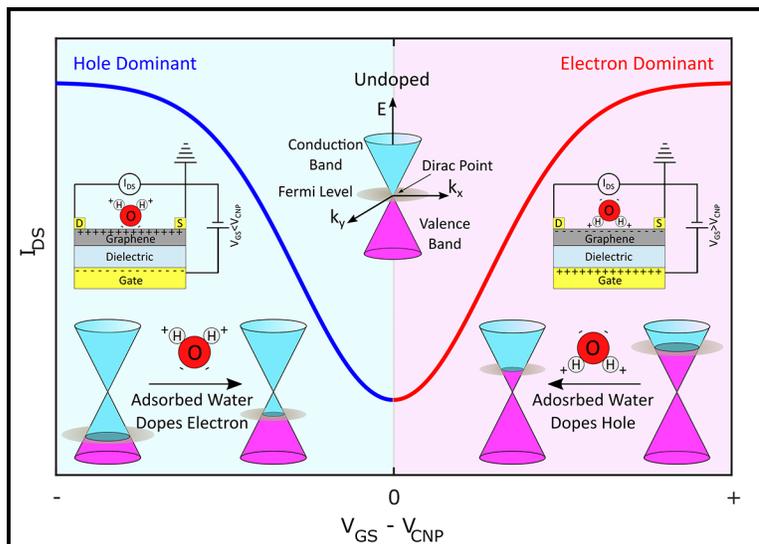


Figure 3:  $V_{GS} = -20V$  was less than  $V_{CNP}$  and the  $V_{CNP}$  shifted in the negative direction, which indicates water is *n*-doping graphene.