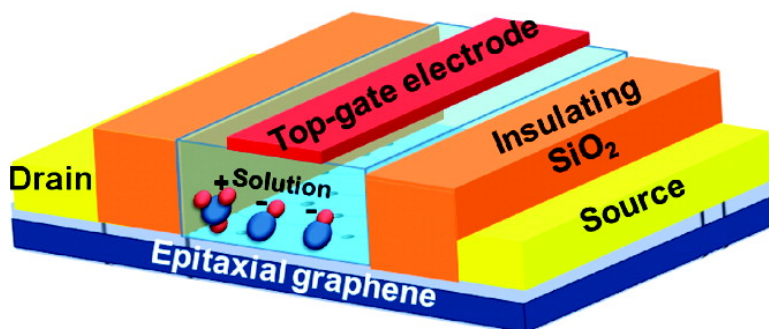


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Solution-Gated Epitaxial Graphene as pH Sensor

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The unique quantum properties of graphene, characterized by its massless Dirac quasiparticles¹ and symmetries of its wave functions, have stimulated intense scientific interest in the material recently.² The high carrier mobilities² of 15 000 cm²/V, ballistic transport, and two-dimensional (2D) nature of graphene make it a promising candidate for applications in ultrafast electronics. In particular, graphene grown epitaxially on SiC substrates and patterned via standard lithographic procedures has been proposed as a platform for carbon-based nano-electronics.³ Epitaxial graphene (EG) can be fabricated on the silicon-terminated (0001) face of high-purity semi-insulating 6H-SiC by thermal desorption of silicon at high temperatures.⁴ Experiments showed that epitaxial graphene shows quasi-ballistic transport and long coherence lengths; properties that may persist above cryogenic temperatures. To achieve field effect response, the gating of the graphene channel is necessary. Because of the thickness of the intrinsic substrate on SiC, only top gating of the epitaxial graphene is feasible currently, in contrast to graphene flakes deposited on silicon oxide where bottom gating is possible. Wu and co-workers⁵ demonstrated that a top-gated few-layer graphene (FLG) using silicon dioxide as gate dielectric showed electron and hole mobilities as high as 5400 and 4400 cm²/V, which is larger than that of SiC or silicon. Alternatively, the top gating can be achieved via “solution gating.” In solution-gate field effect transistor (SGFET), the modulation of the channel conductance is achieved by applying a gate potential from a reference electrode placed on top of the channel, across the electrolyte which now acts as the dielectric. The gate potential induces the build up of ions at the solid/liquid interface; this will alter the surface charge density and can have important consequence for processes such as electron transfer to charged redox species, adsorption of charged molecules, and ion sensitivity. Because of the ambipolar characteristics of graphene, it is anticipated that both hydroxyl (OH⁻) and hydroxonium (H₃O⁺) ions may be able to modulate the channel conductance by doping “holes” or “electrons,” respectively, but this point has not been verified to date. In practice however, the charging process depends on the whether these ions can be specifically bound at the inner Helmholtz plane at the graphene/electrolyte interface. Therefore, to elucidate the charging process at the graphene/electrolyte interface, we investigate the electrochemical double layer of graphene using cyclic voltammetry (CV) and frequency dependent impedance spectroscopy.

The experiments were carried out on two types of few-layer graphene (FLG) samples (1–2 layer and 3–4 layer epitaxial graphene). Details for the fabrication of epitaxial graphene samples have been published.⁶ The preparation of FLG samples of various thickness was monitored using scanning tunneling microscopy and atomically resolved images of single, bilayer, and triple layer EG could be resolved (Supporting Information, S1).

The methods for fabricating the FLG samples for electrochemical studies and SGFET operation in solution are detailed in the

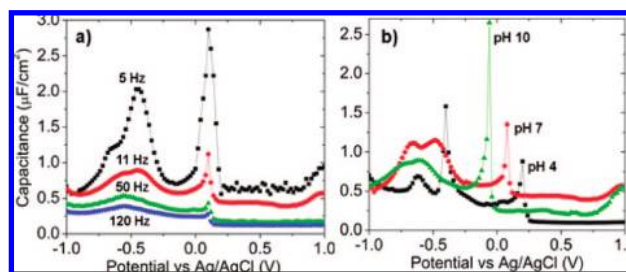


Figure 1. Interfacial capacitance plots of graphene derived from impedance measurements. (a) Frequency dispersion of measured capacitance for adsorbed H₃O⁺ at -0.5 V and OH⁻ at -0.2 V collected in 10 mM KCl/10 mM PBS solution at pH 7. (b) pH dependence of interfacial capacitance peak potential (collected at fixed frequency of 11 Hz).

Supporting Information. Cyclic voltammetry (CV) of the FLG samples was measured in a standard electrolyte of 10 mM phosphate buffer solution with 10 mM KCl. The pH of the solutions was adjusted by adding aliquots of 0.5 M HCl or KOH. In CV, clear maxima in the cathodic and anodic peak currents can be observed (Supporting Information, S2). The positions of the pH-dependent cathodic and anodic peaks agree with the electrochemical potential for the H₂/H₃O⁺ couple (H₂ + H₂O → H₃O⁺ + e⁻) and O₂/OH⁻ couple (O₂ + 2H₂O + 4e⁻ → 4OH⁻). A linear relationship between the anodic (or cathodic) peak heights with the scan rate of the applied potential v was observed, suggesting that these peaks originate from a nonfaradaic (capacitive) process involving the adsorption of ions on the surface. In this case, varying scan rates induces a capacitive charging current, which is proportional to interfacial capacitance, that is, $i_c = C_{int} \times v$, where i_c is the charging current and C_{int} is the interfacial capacitance. To further elucidate the origin of the maxima observed in the CV, frequency-dependent impedance spectroscopy was performed in the potential range from -1.0 to +1.0 V at frequency ranging from 5 to 120 Hz.

Figure 1a shows potential–capacitance plots where capacitance peaks were observed at similar anodic and cathodic peak potentials as CV at +0.2 and -0.5 V, respectively. The frequency dispersion in the vicinity of these potentials suggests a slow ion adsorption/desorption process.⁷ It can be deduced that the anodic and cathodic peak currents are due to redox couples, O₂/OH⁻ and H₂/H₃O⁺, respectively, in which both OH⁻ and H₃O⁺ ions are specifically adsorbed on the graphene surface.⁸ The much sharper OH⁻ capacitance peak observed at +0.2 V compared to the broader feature for the H₃O⁺ peak may imply a more ordered arrangement of the hydroxyl ions in the inner Helmholtz plane of the graphene/electrolyte interface. The pH dependence of these peaks is further corroborated by a direct proportional shift of these peaks with changes in the electrochemical potential of the O₂/OH⁻ and H₂/H₃O⁺ with pH in Figure 1b. For example, the electrochemical potential of the O₂/OH⁻ couple is +0.7 V at pH 4.3 and +0.5 V at pH 7; it can be seen that the OH⁻ peak in the capacitance plot shifted by 0.2 V with pH accordingly. The positions of these peaks

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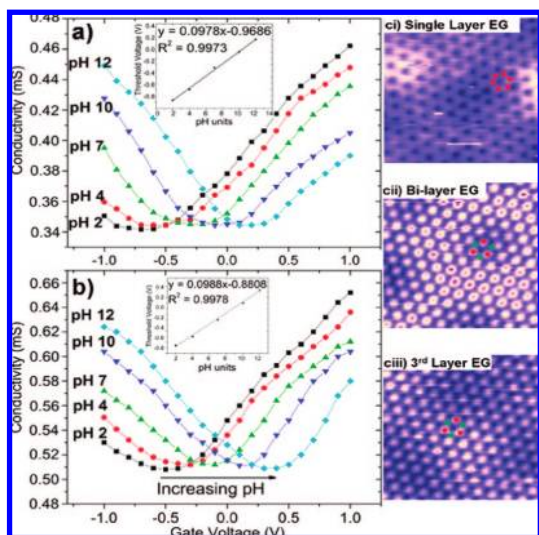


Figure 2. Conductivity versus gate potential plot of a SGFET fabricated on (a) 1–2 layers EG and (b) 3–4 layers EG. The measurements were recorded in 10 mM KCl/10 mM PBS between pH 2 and 12 at constant drain–source voltage of -1 V. The inset shows the plot of shift in threshold voltage ($V_G = E_D$) versus pH, where a supra-Nernstian sensitivity of 99 meV/pH can be obtained. (c) 3×3 nm² STM images of (i) single layer, (ii) bilayer, and (iii) trilayer graphene epitaxially grown on 6H-SiC(0001) with $V_{tip} = 0.1$ V.

are insensitive to changes in ionic strengths or buffer concentrations (Supporting Information, S3).

This indicates that the electrochemical double layer at the graphene/electrolyte interface is very sensitive to pH. The ideally polarizable graphene/electrolyte interface allows the capacitive charging of the surface by H_3O^+ or OH^- , which plays a similar role as the gate potential in changing the Fermi energy. Figure 2 shows the conductivity plot of the graphene SGFET (slope of drain–source current I_{d-s} versus drain–source voltage V_{d-s}), when the gate voltage (V_g) is swept between 1V and -1 V, with the V_{d-s} held constant at -1 V. The transfer characteristics exhibit a “V” shaped p - to n -type transition and the dip in the “V” corresponds to a minimum conductivity of $\sim 4e^2/h$ at the Dirac point (E_D). The mobility of the device can be calculated from the linear regime of the transfer characteristics, $\mu = (1/C_g)(\delta\sigma/\delta V_g)$, where C_g is dominated by the quantum capacitance of graphene (20 nF cm^{-2}).^{9,10} This gives rise to a maximum hole and electron mobility of 3600 $cm^2/(V \cdot s)$ and 2100 $cm^2/(V \cdot s)$ for the 3–4 layer EG, respectively. In the case of 1–2 layer EG, the values are about 15% lower. These mobility values are nearly an order of magnitude higher than carrier mobilities for SGFET devices based on hydrogen-terminated diamond (~ 300 $cm^2/(V \cdot s)$ for holes)¹¹ or silicon (400 for holes and 500 $cm^2/(V \cdot s)$ for electrons).¹² Because of coupling with the SiC substrate, as-prepared EG is usually electron-doped, the energy of the expected Dirac point, E_D , is about 0.4 eV below the Fermi energy.⁴ Interestingly, the conductivity curves for 1–2 layer EG was observed to be displaced more toward the negative gate voltage range ($E_D = -0.3$ eV) compared to 3–4 layer EG ($E_D = -0.1$ eV). Such negative shift is due to the stronger coupling effect with the substrate which gives rise to n -doping in the 1–2 layer EG. For both EG, it can be seen in Figure 2 that as pH increases, the Dirac point shifts toward more positive potential, which is indicative of increasing p -doping of EG by the adsorption of OH^- ions. The parallel shift of the σ - V_g conductivity plots with pH suggests that there is no change in carrier mobilities, that is, minimal scattering of the carriers. Another interesting point is the width of the plateau region at the Dirac point. We note that the width of 0.2 eV is significantly narrower than that reported ~ 10 eV width for the n - p plateau region in SiO₂ top-gated

EG.⁵ We speculate that the more abrupt n - to p - transition in solution-gated graphene may be related to the capacitive charging caused by specifically adsorbed ions.

It is noticed that the application of negative gate potential, which induces the accumulation of OH^- ions on the surface, produces a larger increase in conductivity compared to the positive gate potential (accumulation of H_3O^+) for both EG samples. From the negative gate voltage side of Figure 2, the measured threshold voltage shift with pH yields a value of 98 mV/pH unit for 1–2 layer EG and 99 mV/pH unit for 3–4 layer EG at constant $V_{ds} = -1$ V. Both values are higher than the theoretical maximum predicted by the Nernst limit (59.2 mV/pH unit).¹³ This supra-Nernstian pH sensitivity was observed only with negative gate voltage, which suggests that the mechanism of pH sensitivity may involve an interplay between surface potential modulation by ion adsorption and the attached amphoteric OH^- groups. It has been speculated that minute amounts of OH^- can be preferentially attached to the walls of carbon nanotubes due to hybridization between the unpaired electrons in the p_x orbital of oxygen in OH^- and the p orbital of the carbon atom in CNT, so the more pronounced effect of OH^- in modulating the conductivity in graphene may be related to surface-bound OH species.^{14,15}

In summary, frequency-dependent impedance measurements reveal a potential regime in which OH^- and H_3O^+ adsorption dominates the electrochemical double layer of graphene. We have successfully demonstrated the solution-gating of epitaxial graphene where ambipolar characteristics with a narrow p - n plateau region (~ 0.2 eV) near the Dirac point is observed. Both n and p carriers can be induced by capacitive charging of the ideally polarizable graphene/electrolyte interface, with the negative gated potential region exhibiting supra-Nernstian response to pH. The sensitive response of graphene to surface charge or ion density points to its possible applications in solution-gated, ultrafast, ultralow noise biosensors or chemical sensors

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Supporting Information Available: Additional plots; method details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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