Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information
Molecular detection by liquid gated Hall effect measurement of graphene

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I. FABRICATION PROCESS OF THE GRAPHENE HALL DEVICES

The graphene/SiO_2/Si samples in the study are purchased from Graphenea and Graphene Supermarket. To reduce the time that the graphene was in contact with chemicals during the fabrication, a fabrication process using an image reversal photoresist (TI35ES) was designed. At first, the purchased graphene/SiO_2/Si was annealed at 150 °C in vacuum for 1h to improve the adhesion between graphene and the substrate. A photolithography process was then used to obtain the graphene Hall structures using a TI35ES as the positive photoresist. A subsequent lithography was then conducted to produce the electrode pattern for the Hall structures using a TI35ES as the negative photoresist. This was followed by a metal evaporation step to deposit the contacts. As the Hall measurements were performed in solution, the sample surface (except for the graphene Hall structures and the electrical contacts on the right) was covered by a lithography process using a bio-compatible epoxy-like photoresist (SU-8). To minimize defects, the samples were annealed at 150 °C in vacuum. They were then mounted on printed circuit boards with those contacts wire-bonded. Before the measurements, all the contacts except for the Hall structures (including the wire bonds) were covered by epoxy. Fig. S1 illustrates the fabrication process, where the photograph shows a fabricated device with all contacts covered by epoxy or SU-8 except for the graphene region.

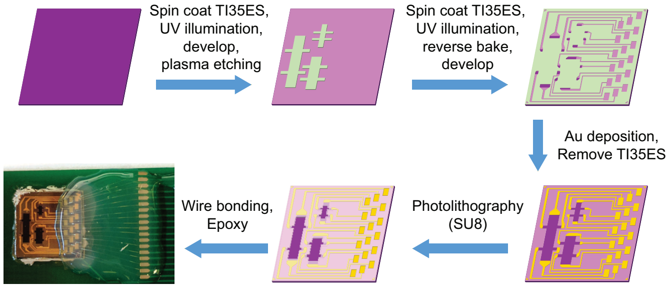

FIG. S1. Fabrication process of graphene Hall structures, where the photograph shows a fabricated device with all contacts covered by epoxy or SU-8 except for the graphene region.

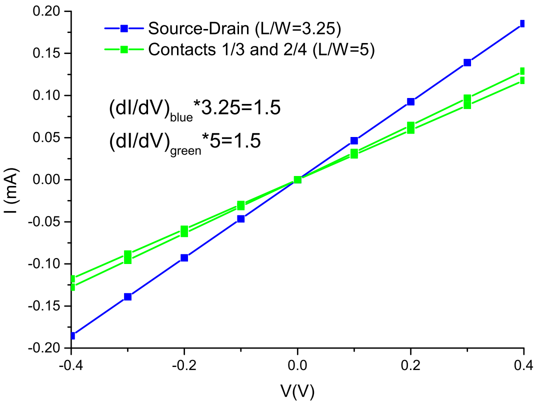

FIG. S2. The linear I-V curve measured on the contacts of a different graphene Hall structure.

II. EXPERIMENTAL SETUP

The gate voltage source and ammeter were provided by a Keithley 6487 Picoammeter/Voltage Source, while the constant current source was a Keithley 6220 Current Source. The applied magnetic flux density is 0.1 T.

A. Electrical test for the contacts on graphene

The experimental setup was carefully checked first by performing the two-probe resistance measurement on the graphene Hall structure using the pico-ammeter and the voltmeter of the setup. The I-V curve measured on different contacts of a graphene Hall structure shown in fig. S2 indicates that the experimental setup is working properly. The connection between all the electrical contacts used in the measurement are perfect Ohmic connections with similar sheet conductance. Therefore, both the graphene device and the power sources behave normally.

B. Hall effect measurement

Sheet resistance is measured using a relation, $\rho_{xx} = \frac{V_{xx}}{I_{DS}} \cdot \frac{W}{L}$. V_{xx} is measured between contacts 3 and 4 in fig. 1(a) in the main text, while V_{xy} between 1 and 3. I_{DS} is the current between the drain and the source contacts, and it is set by the constant current source. $R_H = \frac{V_{xy}}{I_{DS}B}$

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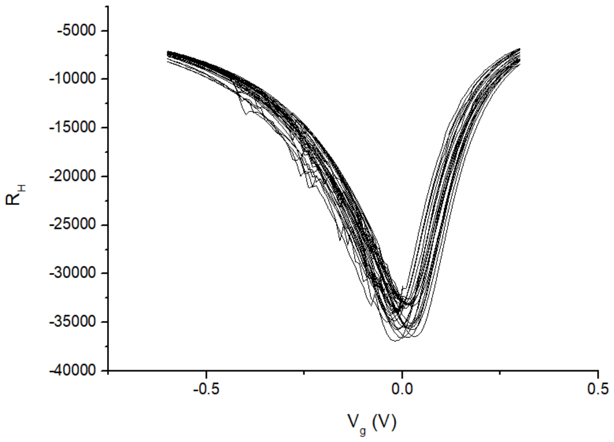

FIG. S3. Repeat measurement of R_H in a PBS solution.

is the Hall resistance, where B is the magnetic flux density.

C. Phosphate-buffered saline solution

Phosphate-buffered saline (PBS) solution is often used in biological studies as it was designed to mimic human body fluid. PBS (1X) has the pH value of 7.4, and it contains NaCl of 137 mM, KCl of 2.7 mM, Na_2HPO_4 of 10 mM, and KH_2PO_4 of 1.8 mM. PBS (10^{-2}X) and PBS (10^{-3}X) were diluted 100 and 1000 times from PBS (1X) using DI water, respectively.

D. Repeat LGHM in a PBS

A graphene Hall device is placed in a PBS with different concentration to repeat the LGHM experiments for more than 20 times. Fig. S3 confirms that the anomalous R_H, which does not change its sign across the "Dirac" point, can be observed consistently.

E. Repeat LGHM in a L-histidine solution

The measurement of R_H of graphene in a solution containing L-histidine shown in fig. 1(c) in the main text is repeated here to test the repeatability of the measurement. The similar response of R_H shown in fig. S4 to that obtained in fig. 1(c) indicates that the LGHM can be used as an effective method for L-histidine detection in the pM range.

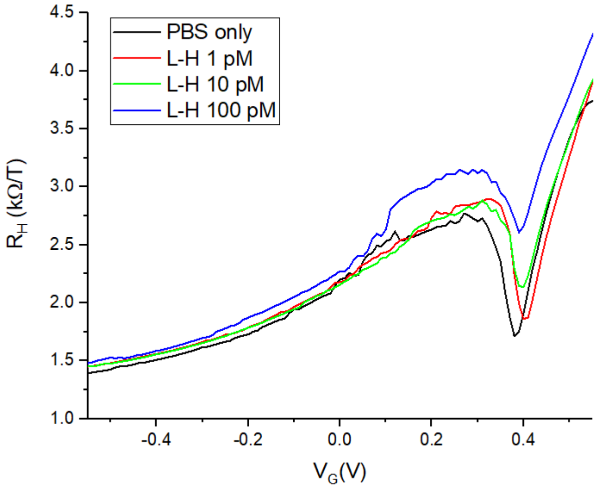

FIG. S4. Repeat measurement of R_H in a L-histidine solution.

III. THEORETICAL ANALYSIS

A. Calculation of Hall resistance

R_H is calculated using the following equation (two-carrier model)[1]

$$R_H = \frac{n_h\mu_h^2[1+(\mu_e B)^2] - n_e\mu_e^2[1+(\mu_h B)^2]}{e[(\mu_e\mu_h B)^2(n_e-n_h)^2+(n_e\mu_e-n_h\mu_h)^2]},$$

where the subscripts h and e denote holes and electrons, respectively, and B is the magnetic flux density.

B. Calculation of capacitance values

In order to determine whether the quantum capacitance is dominant in solution, a 3-step analysis of the PBS (10^{-3} X) system is performed using the data obtained in fig. 3(a) in the main text. Step 1, the empty violet circles are fitted using the two-carrier model to obtain the charge carrier density and the Fermi level. Step 2, the potential drops in graphene (V_Q) are estimated from the Fermi level by $V_Q = -\frac{E_F}{e}$. Thus the potential drop in EDL (φ_{EDL}) can be derived. Step 3, the quantum (C_q), EDL (C_{EDL}), and total (C_t) capacitances are calculated using $C_q = e^2D(E_F)$ (where $D(E_F)$ is the the density of states), $C_{EDL} = e\frac{\mathrm{d}n_{net}}{\mathrm{d}\varphi_{EDL}}$, and $C_t = e\frac{\mathrm{d}n_{net}}{\mathrm{d}V_G}$. The equivalent quantum capacitance is calculated using $e^2\left|\frac{\mathrm{d}n_{net}}{\mathrm{d}E_F}\right|$.

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[1] H. Zhan, *Graphene-Electrolyte Interfaces: Electronic Properties and Applications* (Pan Stanford Publishing, 2018).