

Colossal enhancement of spin-orbit coupling in weakly hydrogenated graphene

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Graphene's extremely small intrinsic spin-orbit (SO) interaction¹ makes the realization of many interesting phenomena such as topological/quantum spin Hall states^{2,3} and the spin Hall effect⁴ (SHE) practically impossible. Recently, it was predicted^{1,5–7} that the introduction of adatoms in graphene would enhance the SO interaction by the conversion of sp^2 to sp^3 bonds. However, introducing adatoms and yet keeping graphene metallic, that is, without creating electronic (Anderson) localization⁸, is experimentally challenging. Here, we show that the controlled addition of small amounts of covalently bonded hydrogen atoms is sufficient to induce a colossal enhancement of the SO interaction by three orders of magnitude. This results in a SHE at zero external magnetic fields at room temperature, with non-local spin signals up to 100 Ω ; orders of magnitude larger than in metals⁹. The non-local SHE is, further, directly confirmed by Larmor spin-precession measurements. From this and the length dependence of the non-local signal we extract a spin relaxation length of $\sim 1 \mu\text{m}$, a spin relaxation time of $\sim 90 \text{ ps}$ and a SO strength of 2.5 meV.

Graphene¹⁰ is an ideal two-dimensional (2D) system with large Young's modulus¹¹ and low bending rigidity¹². Its extraordinary in-plane mechanical strength allows for large out-of-plane deformations, even at the atomic scale. This enables a broad class of chemical reactions/functionalizations, that are not practical with other 2D materials^{13–15}. The out-of-plane distortion of the planar carbon bonds is unique to graphene and may allow for a strong enhancement in its otherwise weak intrinsic SO coupling strength¹. This enhancement is unlike the SO enhancement in metals¹⁶ and semiconductors¹⁷, and is even distinct from the curvature-induced SO coupling in carbon nanotubes^{18,19}. As the sp^3 -bond angle depends strongly on the graphene–substrate interaction, the hydrogenation of graphene allows for a controllable SO strength ranging from a few tens of microelectronvolts up to 7 meV (ref. 1). This allows the manipulation of electron/hole spins in graphene through SHE (refs 17,20–24), thus eliminating the need for any magnetic elements or externally applied (local) magnetic fields in the device architecture.

We introduce small amounts of covalently bonded hydrogen atoms to the graphene lattice by the dissociation of a hydrogen silsesquioxane (HSQ) resist²⁵. The extent of hydrogenation for our samples is determined by Raman spectroscopy measurements^{26,27} (see Supplementary Information) and gives ~ 0.01 – 0.05% hydrogenation for a HSQ dose in the range 0.4 – 5 mC cm^{-2}

(Fig. 1c). Our studies focus on samples that are only weakly hydrogenated, because hydrogen atoms are predicted to cluster at higher densities²⁸. In such samples, our spin-transport measurements both at room temperature and low temperatures show a large non-local signal in the absence of any externally applied magnetic fields. By studying the length, width, adatom density and in-plane magnetic field dependence of the spin signal, we estimate the SO coupling strength (Δ_{SO}), the spin relaxation length (λ_s) and the spin relaxation time (τ_s).

Charge and spin transport measurements are characterized in graphene Hall bar devices (Fig. 1 and see Supplementary Information). The scanning electron micrograph of one such device with multiple Hall bar junctions is shown in Fig. 1a. The room-temperature local resistivity (ρ) and the non-local resistance (R_{NL}) measurements for the exfoliated pristine graphene device S1 with length $L = 2 \mu\text{m}$ and width $W = 1 \mu\text{m}$ are shown in Fig. 2a. The presence of a finite R_{NL} at zero fields is not intriguing, because it is comparable to the estimated ohmic contribution (R_{Ohmic} ; refs 29,30),

$$R_{\text{Ohmic}} = \rho e^{-\pi L/W}$$

However, already after very weak hydrogenation $\sim 0.02\%$, we observe a significant ($\sim 400\%$) increase in R_{NL} (Fig. 2a), well above what can be accounted for by R_{Ohmic} . With increasing hydrogenation the measured R_{NL} shows a steep increase, reaching 170 Ω at 0.05% hydrogenation (Fig. 2b). A strong increase of the R_{NL} is observed even at charge densities $> 1 \times 10^{12} \text{ cm}^{-2}$. These results are reproduced consistently in 18 junctions in 5 samples. As the ohmic contribution to R_{NL} remains negligible over the entire hydrogenation rate (Fig. 2b), the only plausible explanation for the observed physical phenomenon (in the absence of an applied field and at room temperature) is the SHE.

The most direct way to confirm the SHE is to study the in-plane magnetic field sweeps, where only the presence of spin-polarized current can lead to an oscillating signal²⁹. For this geometry the non-local signal has been predicted to oscillate in a magnetic field range given by the Larmor frequency $\omega_B = \Gamma B \leq (D_s/W^2)$ (ref. 29), where Γ is the gyromagnetic ratio, B is the applied magnetic field, D_s is the spin diffusion coefficient and W is the width of the sample. For this, devices with higher mobility (higher D) and smaller W are selected so that the condition $W < \lambda_s$ is satisfied and the variation in the spin polarization across the strip is negligible²⁹. Figure 3 shows the in-plane field dependence of R_{NL} for the device with 0.01%

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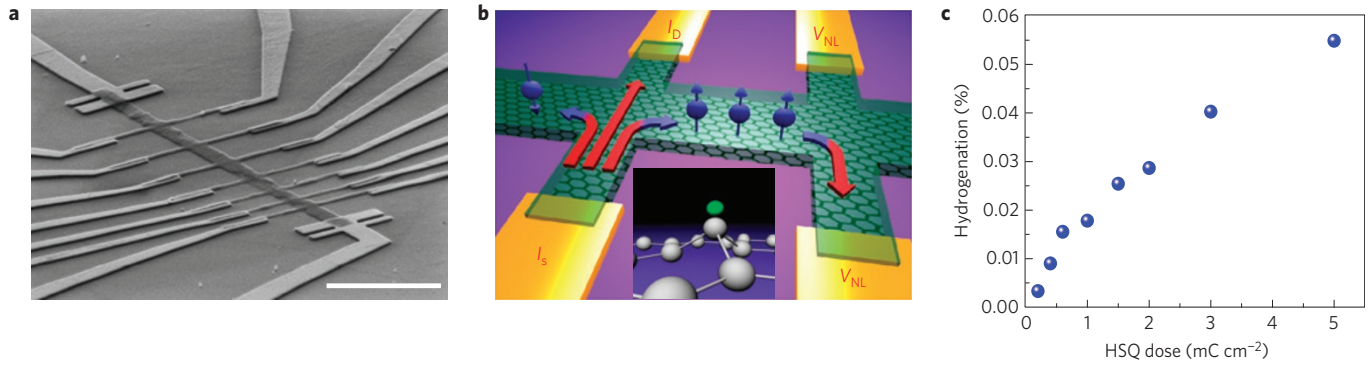


Figure 1 | Device characterization. **a**, Scanning electron micrograph of a hydrogenated graphene sample showing multiple Hall bar junctions. Scale bar, 5 μm . **b**, Measurement schematics for the non-local spin Hall measurement. Inset: schematics showing the deformation of the graphene hexagonal lattice due to hydrogenation. **c**, Evolution of the percentage of hydrogenation with increasing irradiation dose for HSQ (0–5 mC cm^{-2}) calculated from the I_D/I_G ratio of Raman peaks.

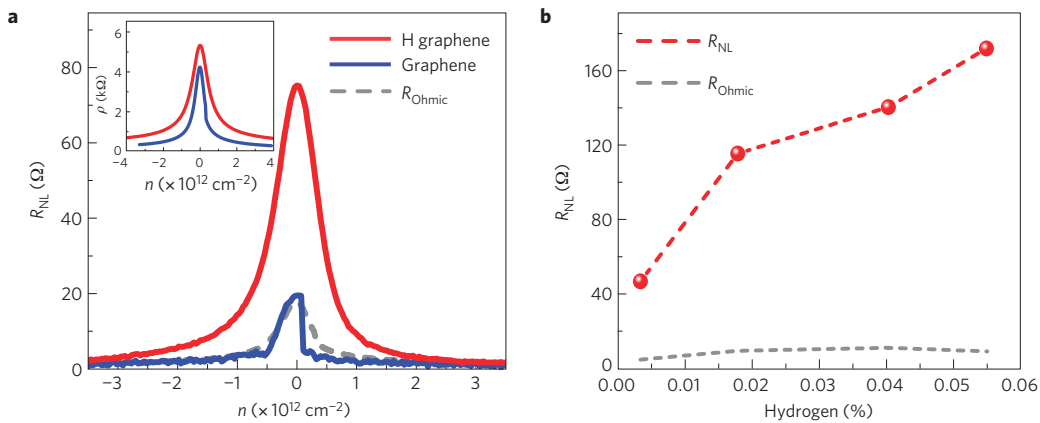


Figure 2 | Room-temperature measurements of non-local signal. **a**, R_{NL} versus n for pristine graphene and hydrogenated graphene at room temperature. The dark grey dashed lines show the ohmic contribution to the measured signal. Inset: ρ versus n for pristine and hydrogenated graphene. **b**, Dependence of the R_{NL} on the percentage of hydrogenation. The dark grey dashed lines show the calculated R_{Ohmic} contribution for this sample.

hydrogenation at $T = 4 \text{ K}$ ($\mu \sim 20,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $L/W = 5$). A fit to this oscillating non-local signal using²⁹

$$R_{\text{NL}} = \frac{1}{2} \gamma^2 \rho W \text{Re} \left[\left(\sqrt{1 + i\omega_B \tau_s / \lambda_s} \right) e^{-\left(\sqrt{1 + i\omega_B \tau_s / \lambda_s} \right) |L|} \right] \quad (1)$$

where γ is the spin Hall coefficient, gives $\lambda_s(B) \sim 1.6 \mu\text{m}$ and $\gamma \sim 0.18$. It should be noted that such an oscillatory behaviour is absent for pristine graphene samples. Thus, the oscillatory behaviour of R_{NL} is a direct signature of both the SHE arising from the hydrogenation of the graphene lattice and the enhancement of an otherwise weak SO coupling strength on hydrogenation.

Further to the magnetic field dependence, we also employed the length and the width dependence to confirm that the origin of the non-local signal in weakly hydrogenated graphene samples is due to the SHE. We first discuss the length dependence by keeping $W = 1 \mu\text{m}$ constant. Figure 4a,b shows the length dependence of R_{NL}/ρ , both at the charge neutrality point (CNP) and at $n = 1 \times 10^{12} \text{ cm}^{-2}$, for the same sample (S3) hydrogenated first to 0.02% and then at 0.05%. The sample has mobilities of $1600 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $900 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for 0.02% and 0.05% hydrogenation respectively. At zero applied field the equation (1) for the non-local signal, for a device with length L and width W , becomes^{29,30}

$$R_{\text{NL}} = \frac{1}{2} \gamma^2 \rho \frac{W}{\lambda_s} e^{-L/\lambda_s} \quad (2)$$

By fitting the R_{NL}/ρ versus L curve using equation (2), we determine $\lambda_s \sim (0.95 \pm 0.02) \mu\text{m}$ and $\gamma \sim 0.58$ at CNP and $\lambda_s \sim (1.12 \pm 0.06) \mu\text{m}$ and $\gamma = 0.45$ at $n = 1 \times 10^{12} \text{ cm}^{-2}$. These results are consistent and in good agreement with the results from conventional lateral spin-valve^{31–34} devices for hydrogenated graphene with ferromagnetic contacts³⁵ (see Supplementary Information for further data).

Next we study the width dependence of the non-local signal at a fixed length $L = 2 \mu\text{m}$ (Fig. 4c, sample S2). After 0.01% hydrogenation S2 still shows a mobility of $14,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature. In such higher mobility samples, the width dependence of the SHE signal shows a power-law dependence. The R_{Ohmic} , on the other hand, depends on the width as $\exp(-\pi L/W)$ and is orders of magnitude smaller. The distinction between R_{NL} and R_{Ohmic} is most apparent at the smallest width (400 nm). This is in good agreement with the theoretical prediction of ref. 29, for narrow channels. The observed width dependence can also be well explained by the theoretical model for clean wires^{36,37}, that is, for high-mobility devices in the limit $W < \lambda_{\text{so}}$, where λ_{so} is the spin-precession length. For most of our width range (0.4–1.8 μm) this condition is easily fulfilled, because for S2 $\lambda_{\text{so}} \sim 8 \mu\text{m}$ (see Supplementary Information).

We next evaluate other key spin parameters such as the τ_s and the Δ_{SO} . In hydrogenated graphene, the dominant spin relaxation is predicted to be the spin dephasing due to Elliott–Yafet scattering¹. In the Elliott–Yafet mechanism, $\tau_s = (\varepsilon_{\text{F}}/\Delta_{\text{SO}})^2 \tau_p$, where ε_{F} is the Fermi energy and τ_p is the momentum relaxation

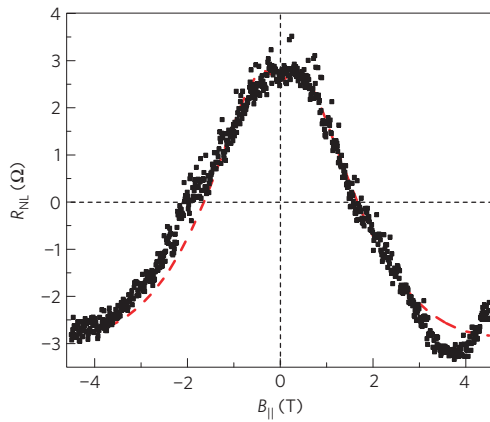


Figure 3 | Magnetic field dependence of R_{NL} . Parallel-field precession data for the sample S2 with $L/W = 5$ and mobility $\sim 20,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. A smooth background has been subtracted from the raw data (see Supplementary Information). The red dotted line is the fit for the experimental curves. The fitting gives $\lambda_s \sim 1.6 \mu\text{m}$.

time^{38,39}. By substituting the value for $\tau_p, \tau_s = \lambda_s^2/D = 90 \text{ ps}$ (D is the diffusion coefficient from the R versus n curve) and the ε_F at $n = 1 \times 10^{12} \text{ cm}^{-2}$, we estimate $\Delta_{SO}^H \cong 2.5 \pm 0.2 \text{ meV}$ for hydrogenated samples. Remarkably this is three orders of magnitude higher than the value predicted for pristine graphene. In such an undistorted graphene lattice, all of the bonds are sp^2 with the σ and π bands orthogonal and separated by energy of the order of $\Delta_E \cong 10 \text{ eV}$. Hence, SO coupling can occur only as a second-order process with energy $\Delta_{SO}^{sp^2} \cong |\Delta_{SO}^{at}|^2/\Delta_E \cong 10 \mu\text{eV}$, explaining the small SO strength in flat graphene⁴⁰. On the other hand, an adatom locally breaks the reflection symmetry across the graphene plane leading to an out-of-plane distortion by an angle φ relative to the plane (it varies from $\varphi = 0^\circ$ for sp^2 , to $\varphi \approx 19.5^\circ$ for a full sp^3). For $\varphi \neq 0^\circ$ the distortion mixes σ and π orbitals that are no longer orthogonal (for full sp^3 these states are degenerate). Hence, the SO interaction becomes a first-order effect leading to a large enhancement of SO coupling for covalently bonded hydrogen impurities in graphene. Following ref. 1, we can show that the strength of the SO coupling can be written as: $r_{SO} = \Delta_{SO}^H/\Delta_{SO}^{at} \cong -3 \tan(\varphi)[1 - 2 \tan^2(\varphi)]^{1/2}$ or equivalently, $\varphi = \text{Arctan}\{[1/4 - (9 - 8r_{SO}^2)^{1/2}/12]^{1/2}\}$. Our experimental results give $r_{SO} \cong 0.25$, which implies $\varphi \approx 5^\circ$. This value is of the same order of magnitude as the value predicted theoretically, $\varphi_{DFT} \approx 16^\circ$,

by *ab initio* calculations for suspended graphene⁴¹. We assign the difference between the measured value and the one obtained by density function theory (DFT) to the interaction between graphene and its substrate⁴⁰, which is not taken into account in *ab initio* methods.

In the presence of this local SO coupling two new terms can be added to the Hamiltonian $H_0 = -i\hbar v_F \sigma \cdot \nabla$, where σ are Pauli matrices that act on the subspace of the sublattices A and B, v_F is the Fermi–Dirac velocity ($\sim 10^6 \text{ m s}^{-1}$) and ∇ is the gradient operator: a Dresselhaus term, $H_D = \lambda_D \sigma_z s_z \tau_z \delta(\mathbf{r}) a^2$, where $\tau_z = \pm 1$ represents either the K or K' points (a is the lattice spacing); and a Rashba term, $H_R = 2\lambda_R (\sigma_x s_y \tau_z - \sigma_x s_y) \delta(r) a^2$. Note that H_D is invariant under time-reversal symmetry, T ($T: \sigma \rightarrow \sigma, T: s \rightarrow -s, T: \tau \rightarrow -\tau$) and parity, P ($P: \sigma \rightarrow -\sigma, P: s \rightarrow s, P: \tau \rightarrow -\tau$). For a uniform system, it opens a gap in the spectrum of size λ_D . H_R is allowed in this case because reflection symmetry is broken. In a uniform system, this term does not open a gap but it splits the up and down spin bands into four hyperbolic bands of energy $E_R(k) = \pm \lambda_R \pm [\lambda_R^2 + v_F^2]^{1/2}$ that are parabolic at low energies with an effective mass given by $m^* = \lambda_R/v_F^2$. These two terms are allowed by symmetry and, in a scattering process, lead to a spin precession and hence to SHE.

Finally, we identify the dominant microscopic mechanism for the observed spin Hall scattering⁴². For the side-jump mechanism the spin Hall resistivity ρ_{SHE} is independent of n_{imp} , whereas for the skew-scattering mechanism $\rho_{SHE} \propto n_{imp}$ (ref. 42). The spin Hall resistivity ρ_{SHE} is estimated from $\gamma = (\rho_{SHE}/\sigma_G) = (\rho_G/\rho_{SHE})$ and gives a value of $\rho_{SHE} = 12.9 \text{ k}\Omega$ and $14.2 \text{ k}\Omega$ for 0.02% and 0.05% hydrogenation, respectively. The value of ρ_{SHE} , thus, depends only weakly on n_{imp} ($n_{imp} \sim 0.9 \times 10^{12} \text{ cm}^{-2}$ for 0.02% and $1.6 \times 10^{12} \text{ cm}^{-2}$ for 0.05% hydrogenation) and hence suggests the dominance of the side-jump mechanism in hydrogenated graphene samples⁴².

We have demonstrated that the SO interaction in graphene can be markedly enhanced by introducing a small concentration of covalently bonded adatoms, without a significant suppression of the conductivity. Hydrogenated graphene has been used as a model system to demonstrate that this leads to a strong SHE. The SHE is confirmed by the non-monotonic oscillatory behaviour of the non-local signal in an applied in-plane magnetic field and also by the length, width and adatom density dependence of the non-local signal. From the length dependence of the non-local signal, we extract a spin relaxation length of $\sim 1 \mu\text{m}$, a spin relaxation time of $\sim 90 \text{ ps}$ and a SO interaction strength of $\sim 2.5 \text{ meV}$ for samples with 0.05% hydrogenation. These findings are crucial for the development of graphene-based spintronics applications, as the need for magnetic elements is eliminated from the device

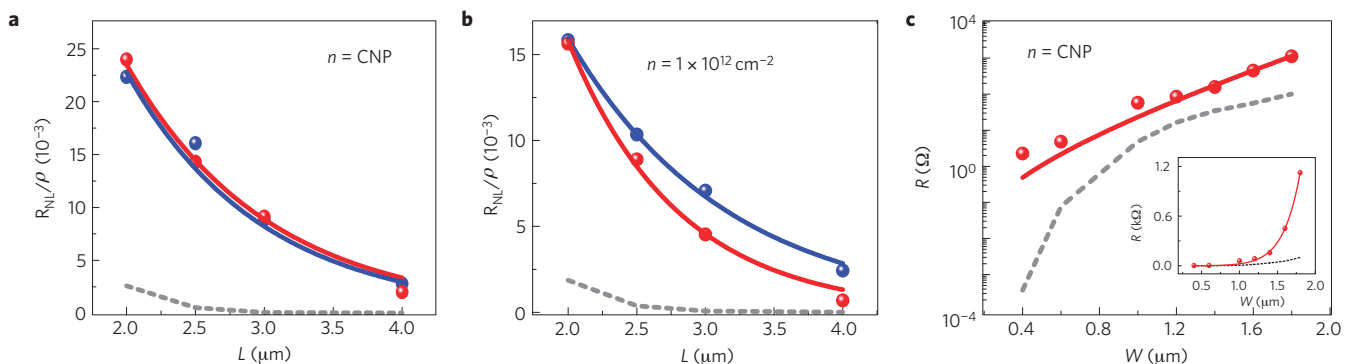


Figure 4 | Length and width dependence of R_{NL} at room temperature. **a, b**, At the CNP (**a**) and at $n = 1 \times 10^{12} \text{ cm}^{-2}$ (**b**) for samples with 0.02% (red solid circles) and 0.05% (blue solid circles) hydrogenation. Here the length is the centre–centre distance between the injector and detector electrodes. The solid lines are the fit for the data and the dark grey dashed line is the calculated ohmic contribution at these charge carrier densities. **c**, R_{NL} (red circles) as a function of width W ($W = 400 \text{ nm} - 1.8 \mu\text{m}$) for a fixed length L ($2 \mu\text{m}$). The solid red line is the fit for the data and the dark grey dashed line is the calculated ohmic contribution (inset: R versus W on a linear scale).

architecture. Last but not least, the demonstration of the non-local SHE due to impurity adatoms in graphene is a major step in the realization of a robust 2D topological states⁶ and a SHE-based spin transistor at room temperature.

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Author contributions

B.Ö. devised and supervised the project. J.B. and B.Ö. designed the experiments. J.B. and G.K.W.K. performed the experiments. A.H.C.N. provided the theoretical work. All authors carried out the data analysis and discussed the results. J.B., A.H.C.N. and B.Ö. co-wrote the paper.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to B.Ö.

Competing financial interests

The authors declare no competing financial interests.