Valley–spin blockade and spin resonance in carbon nanotubes

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The manipulation and readout of spin qubits in quantum dots have been successfully achieved using Pauli blockade, which forbids transitions between spin-triplet and spin-singlet states. Compared with spin qubits realized in III–V materials, group IV materials such as silicon and carbon are attractive for this application because of their low decoherence rates (nuclei with zero spins). However, valley degeneracies in the electronic band structure of these materials combined with Coulomb interactions reduce the energy difference between the blocked and unblocked states, significantly weakening the selection rules for Pauli blockade. Recent demonstrations of spin qubits in silicon devices have required strain and spatial confinement to lift the valley degeneracy. In carbon nanotubes, Pauli blockade can be observed by lifting valley degeneracy through disorder, but this makes the confinement potential difficult to control. To achieve Pauli blockade in low-disorder nanotubes, quantum dots have to be madeultramall, which is incompatible with conventional fabrication methods. Here, we exploit the bandgap of low-disorder nanotubes to demonstrate robust Pauli blockade based on both valley and spin selection rules. We use a novel stamping technique to create a bend nanotube, in which single-electron spin resonance is detected using the blockade. Our results indicate the feasibility of valley–spin qubits in carbon nanotubes.

Two quantum dots containing two electrons in total can be tunnelled to the transition between two charge states—(1,1) with one electron in each dot and (2,0) with both electrons in the first dot. The transition involves tunnelling of the electron from the second to the first dot. Even when this transition is allowed energetically, it can be blocked by selection rules. In III–V quantum dots (for example, GaAs or InAs), a blockade can be set up between a (1,1)-triplet state and a (2,0)-singlet state. Important for a robust blockade is the condition that the (2,0)-triplet state be high in energy, because this excited state is not blocked by selection rules. The crucial energy difference, $E_{2T}-E_{1T}$, between the (2,0)-triplet and (2,0)-singlet states can be several meVs in III–V materials. In carbon nanotubes the two-electron states are grouped into singlet-like and triplet-like states. The energy difference, $E_{ss}$, between the singlet-like and triplet-like states can be one or two orders of magnitude smaller than in III–V materials. There are two main reasons for this: additional levels from valley degeneracy and stronger Coulomb interactions in the carbon nanotubes. These complications have prevented a consistent observation of Pauli blockade and, as a result, spin manipulation has not been realized. We avoid these complications by using the large level spacing from the bandgap of the nanotube and demonstrate a robust valley–spin blockade. Here, we discuss our novel fabrication method for obtaining ultraclean quantum dots controlled by a set of gate electrodes with a high-frequency bandwidth.

Two approaches are usually used to fabricate nanotube quantum dot devices: deposition of contacts and gates after a nanotube is grown and located on a substrate, or growing a suspended nanotube over predefined contacts and gates. The second approach eliminates contamination of the nanotube by chemical processing, creating an ultraclean nanotube device. However, the high growth temperature limits the choice of materials and device design, limiting the devices to having large gate spacings and thus a quantum dot confinement insufficient to overcome Coulomb interaction effects.

To create ultraclean double quantum dots with optimal confinement, we have developed a novel stamping technique, following the pioneering work by Wu et al. We transfer the nanotube from the growth chip to the device chip under ambient conditions. The thickness of the device contacts is optimized so that, in most devices, the centre of the nanotube touches the trench bottom, resulting in a bend (Fig. 1b), which is proposed to be necessary for electrically driven spin resonance. Five gate electrodes are embedded underneath the nanotube. A double dot potential is created by the combination of Schottky barriers at the contacts and voltages applied to the gates. By tuning these gate voltages, we can populate each dot with a well-defined number of electrons or holes.

The device exhibits ambipolar double quantum dot behaviour, as seen from the charge stability diagram of Fig. 1c, where current through the double dot is measured as a function of the outermost gate voltages. Depending on the gate voltages, we can configure the device in a p–n, n–n, n–p or p–p region and determine the exact charge occupation number of each dot. For each region, we can find Coulomb blockade features exhibiting a characteristic fourfold periodicity of addition energy in both quantum dots, indicating shell-filling of electrons and holes. The first shells of electrons and holes are separated by a 30 meV bandgap.

The key signature of Pauli blockade is current suppression for one direction of the source–drain bias. In our device, blockade becomes most evident with the double dot tuned into the p–n region. This is shown in Fig. 2a,b, where we observe multiple triple point bias triangles with a suppressed current at the baseline depending on bias direction. As expected, blockade is observed for transitions where, in the initial configuration, both dots contain an odd number of electrons.

A robust Pauli blockade requires a large $E_{2T}$, as conventionally provided by a strong dot confinement. Here, we exploit the high tunability of our double dot to obtain a particularly large $E_{2T}$ that includes the bandgap of the nanotube (Fig. 2c). We focus on the $(3h,1e)$ → $(2h,0)$ transition, where both shells initially contain one electron. Taking account of both valley ($K$ or $K'$) and spin ($\uparrow$ or $\downarrow$) quantum numbers, each shell contains four states, denoted $K_\uparrow$, $K_\downarrow$, $K'_\uparrow$ and $K'_\downarrow$. Spin–orbit coupling splits each shell into two doublets with energy difference $\Delta_E$ at zero magnetic field. For negative bias (Fig. 2d), current flows as either of the two electrons in the left dot can tunnel to the empty shell on the right. At positive bias (Fig. 2e), assuming that valley and spin are conserved during tunnelling, current is blocked when the initial and final states

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Figure 1 | A carbon nanotube double quantum dot fabricated by stamping. a, Device schematic and stamping technique. A suspended carbon nanotube is grown between pillars on a transparent quartz substrate. This growth chip is optically aligned over the device chip and brought into contact so that the nanotube bridges source and drain contacts (yellow). Five local gates (red) embedded in an insulating layer control the electron/hole number and the tunnel rates of the double quantum dot. b, Scanning electron micrograph (taken at 75° inclination) of a device similar to the measured device, showing a single nanotube with a bend. c, Current as a function of the left and right gate voltages $V_L$ and $V_R$ at a source–drain bias of $V_{SD} = 1$ mV. Regularly spaced Coulomb peaks show clear double quantum dot transport behaviour over a large gate space. Individual electrons (holes) are added in n- or p-type quantum dots depending on the gate settings. Schematic energy diagrams illustrate four types of double quantum dot configuration. A characteristic fourfold periodicity of addition energy is visible, revealing the filling of four-electron shells. Green circles in the n–p region indicate double quantum dots with filled shells in both dots.

Figure 2 | Valley-spin blockade in a p–n double quantum dot. a, b, Current at triple point bias triangles in a few-charge p–n double quantum dot at negative (a) and positive (b) bias. The triangles marked by dashed circles (squares) show a suppressed current at the baseline in a (b) compared with the same triangles in b (a). Numbers in brackets denote the occupation of the left and right dot, with h and e indicating holes and electrons, respectively. c, Energy levels of the first shells of electrons and holes. Spin–orbit coupling splits a shell of four electrons (blue) or holes (white) into two levels with energy difference $\Delta_{SO}$. A particularly large shell spacing $\Delta E_{shell}$ separates the first hole shell from the first electron shell across the bandgap. Dashed levels indicate the nearest higher shell if there were no bandgap. d, e, Schematics of the energy levels for the transitions between (2h,0) and (3h,1e). For the non-blockaded bias direction (d), either of the two electrons in the left dot can tunnel to the empty shell in the right dot. For the blocked bias direction (e), electron with state $K'$ in the right dot cannot tunnel to the left dot due to valley-spin conservation. f, g, Measured current for the non-blockaded bias direction illustrated in d. g, Current measured for the opposite bias direction. (Dashed lines mark the position of the triangles.) Suppressed current (compared with f) across the entire triangles is the signature of valley-spin blockade. f and g correspond to the square regions in a and b with the same colours.
differ in either valley or spin quantum numbers. The blockade is lifted when the interdot energy detuning is large enough that the initial state has access to additional final states involving a higher shell. However, as the nearest higher shell in the left dot is across the bandgap, this situation does not arise with a 10 mV bias (Fig. 2g). In the case of only spin blockade, the blockade is lifted as soon as the initial state has access to an empty final state with the same spin. Spin blockade would happen if the disorder-induced valley-mixing term $\Delta_{KK'}$ differed between the left and right dots\(^{21}\). To lift valley-spin blockade, the empty final state must have both the same valley and spin, leading to an additional valley selection rule for interdot tunnelling. This additional selection rule leads to suppression of the current across the entire triangles in Fig. 2g. This current suppression, which, in contrast to spin blockade, continues even when transport occurs via excited states of the left dot, is the unambiguous signature of valley–spin blockade.

In Fig. 3, we investigate valley and spin relaxation by measuring the leakage current for different orientations of the magnetic field. We consider the valley–spin blockaded triangles shown in Fig. 2g with the detuning axis marked by the black arrow. Figure 3a shows the leakage current as a function of detuning and magnetic field $B_z$ along the $z$-axis. The leakage current is due to valley–spin relaxation and can arise from spin–orbit interaction\(^{6,12,20,22}\), intervalley scattering\(^{23}\) and hyperfine interaction with the $\sim 1\% ^{13}$C lattice nuclei\(^{12}\).

Three transitions, mediated by valley–spin relaxation, are identified using a two-electron double dot model (Fig. 3a,b). For simplicity, we model the charge states $(3h,1e)$ as $(1,1)$ and $(2h,0)$ as $(2,0)$, and ignore the higher shells in the left dot that remain empty in our experiments. Valley ($v$) and spin ($s$) together lead to 16 two-electron states, grouped into six valley–spin antisymmetric (singlet-like ($S$)) states with both electrons in one shell, and ten symmetric (triplet-like ($T$)) states for which two shells are required\(^{24-26}\). These 16 linearly independent states are listed explicitly in Supplementary Section S1. We write these states with the following shortened notation

$$\vert (1,1) + \phi \rangle, \quad \vert (2,0) + \phi \rangle, \quad \vert (2,0) - \phi \rangle, \quad \vert (2,0) - \phi \rangle, \quad \vert (2,0) - \phi \rangle, \quad \vert (2,0) - \phi \rangle, \quad \vert (2,0) - \phi \rangle, \quad \vert (2,0) - \phi \rangle, \quad \vert (2,0) - \phi \rangle, \quad \vert (2,0) - \phi \rangle, \quad \vert (2,0) - \phi \rangle, \quad \vert (2,0) - \phi \rangle, \quad \vert (2,0) - \phi \rangle, \quad \vert (2,0) - \phi \rangle, \quad \vert (2,0) - \phi \rangle, \quad \vert (2,0) - \phi \rangle.$$
s(T)\nu_1\nu_2\nu_3\nu_4 = (\nu_1\nu_2\nu_3\nu_4)\mu (n, normalization factor).

We use the lowest energy \(TK\downarrow K\uparrow (1,1)\) state as a spectroscopic probe to measure the \((2,0)\) spectrum\(^{27}\). The measured transitions (dashed lines in Fig. 3a) are in good agreement with the calculated spectrum. The calculation incorporates two parameters: \(\Delta_{SO} = 1.6\) meV, measured by the difference in transition detunings at zero field (the large \(\Delta_{SO}\) has been observed in multiple devices and is the subject of ongoing investigation), and orbital magnetic moment \(\mu_{orb} = 0.9\) meV T\(^{-1}\), measured by the slope of the transitions with the field. (Note that the slope of the transitions changes at 2.2 T, presumably because the \((1,1)\) ground state changes at that field.) Six valley–spin relaxation transitions are possible, but only three are observed. The relaxation rates that determine which transitions are visible in the data are not fully understood. (For further discussions, see Supplementary Section S2.)

The orbital magnetic moment pointing along the nanotube axis leads to a large g-factor anisotropy. When varying \(B_y\) (Fig. 3a), we couple to both the orbital magnetic moment and to the Zeeman energy, and the two transitions therefore have much larger slopes than when varying \(B_x\) (Fig. 3c), where we only couple to the spin. Figure 3f shows the current as a function of field angle for fixed \(|B| = 2\) T. The measured transitions show excellent agreement with a model incorporating the g-factor anisotropy.

An interesting consequence of the level structure in nanotubes is that valley–spin blockade appears also for the initially unblocked bias direction at finite \(B_y\). When the magnetic field induces a ground state crossing from \(SK\downarrow K\uparrow (1,1)\) to \(TK\downarrow K\uparrow (1,1)\) the current becomes blocked\(^{26}\). This is evident in Fig. 3d inside the region indicated by the purple circle, and the corresponding levels are illustrated in Fig. 3e.

In Fig. 4, we explore the consequences for magnetotransport of the bend expected in this device. Figure 4a shows the leakage current anisotropy when a magnetic field is rotated in the x-y plane. Current near zero detuning is more suppressed when the field is pointed along the y-axis. This can be explained by considering that at low detuning transport only proceeds via single-particle states \(K\downarrow\) and \(K\uparrow\). This doublet forms an effective spin-1/2 system governed by a Zeeman field\(^{20}\) \(B_{eff} = g\mu_B B/2\), which, due to the bend, can be different in the two dots. The effective spins in the two dots precess about these different \(B_{eff}\) axes so that an initially parallel effective spin state acquires an antiparallel component. This causes lifting of the valley-spin blockade, resulting in a higher leakage current. However, in the z-y plane the projection of the nanotube is straight. Thus, when \(B_y\) is applied, \(B_{eff}\) is the same in
both dots and valley–spin blockade remains. As expected, the current is isotropic for the unblockaded bias direction (Fig. 4c).

The observation of valley–spin blockade in a bent nanotube allows the detection and driving of electric dipole spin resonance (EDSR). We use a microwave-frequency signal added to \( V_z \) to oscillate electrons in the double dot. Figure 4e shows the current as a function of \( B_z \) and microwave frequency at a blockaded transition in the many-electron regime of a second device. When the frequency of the microwave matches the splitting of two valley–spin states, the blockade is partly lifted. EDSR is observed as V-shaped lines with slopes yielding \( g \approx 2 \). The relatively small \( g \)-factor in this second device is presumably due to a large electron occupation or disorder.\(^{28}\) EDSR is also detected in the first device in a different cooldown, with the rather complex spectrum shown in Supplementary Section S7.

In summary, we have developed a new fabrication method to make a double quantum dot in a bent carbon nanotube using a stamping technique. The devices exhibit an exceptional confinement and tunability, which enable us to observe valley–spin blockade and to demonstrate electric dipole spin resonance. Our findings open a path towards qubit manipulation in carbon nanotubes.

**Methods**

Fabrication included the carbon nanotube growth chip and the device chip. On the growth chip, pillars with a height of \( \approx 5 \mu m \) were fabricated using electron-beam lithography and plasma-enhanced dry etching on a double-side polished quartz wafer. Mo/Fe catalyst was deposited on top of the pillars, and nanotubes were grown by chemical vapour deposition. In \( \approx 10 \%) of devices, a single tube spanned between the pillars. On the device chip, a silicon substrate covered with 1.9 \( \mu m \) thermal oxide was dry-etched to create a mesa \( \approx 1 \mu m \) tall. A 5/10 nm Ti/Au gate layer was deposited on the mesa, followed by atomic layer deposition of 60 nm Al\(_2\)O\(_3\) as the gate insulator. On top of this, a 5/80 nm Ti/Au layer was deposited for the contacts. A contact aligner (Karl Suss MJB-3) was used to transfer the nanotube from the growth chip to the device chip with a transfer success rate close to 100%. The first measurements (Fig. 1c) were carried out in a 4 K helium dewar. EDSR was measured at 260 mK, and other measurements were performed in a dilution refrigerator with a base temperature of 100 mK. For the measurement in Fig. 4f, the applied microwave power was \( \approx 41 \) dBm and \( V_{SD} \approx 5 \) mV.

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**References**


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**Author contributions**

F.P. fabricated the devices. F.P. and E.A.L. performed the experiments. I.P.K. supervised the project. F.E.P., E.A.L. and L.P.K. prepared the manuscript. All authors discussed the results and commented on the manuscript.

**Additional information**

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**Competing financial interests**

The authors declare no competing financial interests.