Reversible spin storage in metal oxide—fullerene heterojunctions

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We show that hybrid MnOx/C60 heterojunctions can be used to design a storage device for spin-polarized charge: a spin capacitor. Hybridization at the carbon-metal oxide interface leads to spin-polarized charge trapping after an applied voltage or photocurrent. Strong electronic structure changes, including a 1-eV energy shift and spin polarization in the C60 lowest unoccupied molecular orbital, are then revealed by x-ray absorption spectroscopy, in agreement with density functional theory simulations. Muon spin spectroscopy measurements give further independent evidence of local spin ordering and magnetic moments optically/electronically stored at the heterojunctions. These spin-polarized states dissipate when shorting the electrodes. The spin storage decay time is controlled by magnetic ordering at the interface, leading to coherence times of seconds to hours even at room temperature.

INTRODUCTION

Promising platforms for future quantum technologies make use not only of the charge of electrons but also their spin angular momentum. This allows the design of storage media controlled by spin polarization and devices for low-power electronics operated via spin currents with no Joule heating, adding as well functionality for sensing, mechanical, heat, and voltage converters, and in optoelectronics (1–8). Carbon-based molecules are of interest because of the small spin-orbit coupling of light elements and a lack of hyperfine interaction in 13C, leading to long spin coherence and diffusion times—the interval before an electron spin changes its direction. However, as far back as 2011, it was realized that molecular spintronics faced challenges when replicating effects exported from conventional crystalline devices due to bad reproducibility, low carrier mobility, and degradation (9). Nevertheless, molecular spintronics has remained a fruitful field of research because of the various novel behaviors and effects, unique to molecular systems and, in particular, interfaces, that can be exploited in multifunctional devices (3, 9, 10). Over the last decade, there has been a concerted effort to comprehend the complex spin-dependent charge interactions between molecules and metals, in particular the formation of spin-polarized interfaces and tunable surface states, where molecular materials offer unique behavior and tunability that can be exploited to produce multifunctional devices via charge transfer and hybridization when in contact with other materials (11–15). The possibility of storing spin angular momentum at room temperature over long timescales in scalable, stable, and optoelectrically control-
The first C60 layer in controns (Fig. 2B, top, and figs. S3 to S6) ([39]) region of the DOS and with conducting states for majority spin electrons, while the Fermi energy for minority spin electrons lies in an empty region of the DOS. This is equivalent to ~0.5 to 1 e\(^-\) per interface cage. Upon addition of 0.6 e\(^-\) to the metallic interface states (table S2) ([20]), DFT simulations show that the molecular orbital states for the C60(2nd) layer are downshifted in energy by 0.5 to 1 eV (Fig. 2B, bottom), in good agreement with the measured LUMO to LUMO* shift (Fig. 1). Surface oxygen preferentially bonds to C60, creating a strong interfacial dipole and rectifying barrier (Fig. 2C). The LUMO shift takes place due to the formation of this dipole, although 98% of the stored charge is localized at the C60(1st) layer. DFT calculated spin-resolved charge density maps when 0.6 e\(^-\) charge is added to the interface, with larger trapping of minority spin electrons at the C60 metal oxide sites, are shown in Fig. 2D. The magnetic moment of C60(1st) in the neutral configuration is 0.05 \(\mu_B\) per cage, increasing to 0.18 \(\mu_B\) once the interface is charged. The moment in C60(2nd) is 0.0 \(\mu_B\) before and after charging.

Wide-field TEM images show that the sputtered Co layer is polycrystalline, with each grain several tens of nanometers in size (Fig. 3A). Although ideal, uniformly magnetized two-dimensional films have a nil demagnetization factor and no stray field, there will be magnetization discontinuities at these grain boundaries. These stray fields lead, e.g., to muon spin depolarization in the vicinity of a ferromagnetic film. In the MnO\(_x\) layer, the magnetism is confined to the surface, and junctions with a CuO\(_x\) electrode replacing MnO\(_x\) do not show dichroism (figs. S7 and S8) ([20]). If the long spin coherence time of trapped charge measured via XMCD is linked to the stabilization of minority spins via stray fields from Co grains, introducing magnetic disorder in the Co layer will break the spin alignment and reduce charge trapping (Fig. 3B). We test this by measuring photocurrents.
Fig. 2. Interface modeling. (A) Top: High-resolution cross-sectional TEM image of a Co(5)/C60(20)/MnOx(10) junction. Inset: Fast Fourier transform (FFT) of the region indicated shows peaks in the diffraction pattern due to nanocrystalline grains in the sublimed C60 film. Bottom: Elemental chemical analysis of the interface—note the Gaussian profile of the e-beam (~10 nm full width at half maximum). The oxygen-to-manganese ratio is ~2:1 close to the C60 interface. (B) Spin-polarized density of states (PDOS) in the neutral (top) and with 0.6 e\(^{-}\) added to the C60 interface (bottom). The formation of a C60-O bond at the surface leads to a strong interfacial dipole and the generation of half-metallic interface states. (C) Changes in the charge density with respect to the neutral system along the direction perpendicular to the interface plane (z). The profile reveals the formation of a dipole layer density (\(\mu_{s}\)) owing to accumulation of negative charge at the C60/\(\beta\)-MnO\(_2\)(110) junction, and positive charge on the opposite side of C60(1st) toward C60(2nd). (D) Computed change in total charge density after 0.6 e\(^{-}\) are added to the C60 interface (|\(\Delta\rho\)| = 10\(^{-6}\) eÅ\(^{-3}\)) for the oxidized, chemically bound minima for spin-up and spin-down states.

Fig. 3. Spin stabilization facilitated by stray fields. (A) Wide area TEM image showing the presence of grains some ~50 to 100 nm in lateral size. (B) Schematic for the stray field \(\mu_{o}H_{s}\) generated by Co grains and the buildup of spin-polarized trapped charge via photocurrents. (C) Photocurrent in Co(5)/C60(20)/MnOx(10) devices as a function of the magnetic history. Lower remanent magnetization leads to less efficient charge trapping and therefore a higher photocurrent. (D) Discharge of the open-circuit voltage (\(V_{OC}\)) under a series of in-plane magnetic fields \(\mu_{o}H_{s}\). The discharge time \(\tau\) is up 30% faster at the coercive field, when the magnetization of the cobalt film is nil. (E) The magnetic field dependence of \(\tau\) follows the anisotropic magnetoresistance (AMR) of the Co electrode, showing the correlation between Co magnetization and spin-polarized charge storage (blue line is a guide to the eye).
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Fig. 4. Magnetic field effects and schematic of the trapped spin capacitor mechanism. (A) Top: XMCD for the initial, charged (floating), and discharged (ground) states in a Co/Al2O3/MnOx junction showing spin-polarized trapped charge. Bottom: NEXAFS in remanence after OOP magnetic fields (Bz). The 283 eV LUMO* peak is displaced toward the pristine LUMO until the Co electrode is magnetically saturated OOP. (B) Decay time constant τ for optically charged junctions, typically ~30 to 300 s for 100 x 100 μm² junctions (fig. S11) (35). The dependence of τ on Hs is similar to that of the TEY at the pristine 284 eV LUMO position. (C) Schematic for spin capacitance. Top: Minority electrons are trapped when the quantization axis C60 layer (α) is parallel to that of the C60/MnOx interface (α’). Bottom: When α = α’, the conductivity G is above zero for both spins. In particular, for α ≠ α’, both spin orientations in C60(2nd) transfer to the interface majority band with the same probability and conductivity (≠0).

generated in MnOx(5)/C60(20)/Co(t) junctions at different magnetic states: in remanence after a saturation in-plane field (remanent magnetization Mr ~90% of saturation, Ms), after an out-of-plane (OOP) field (Mr ~0.2 Ms), and after demagnetizing the film with an oscillating damped field (Mr ~0) (fig. S9) (7, 20). When M~Ms, the stray field is uniform and stabilizes the spins in the opposite direction to the Co and MnOx magnetization. The minority spin charge is trapped at the interface due to a lack of available spin-down states to diffuse into, reducing the photocurrent. When the electrodes are disordered, the stray field does not necessarily stabilize the spin direction opposite to the MnOx magnetization, and charges abandon the traps via thermal fluctuations—the energy depth of the traps being of the order of tens of megaelectron volts (fig. S10) (35). The photocurrent is then increased in this magnetically disordered state by up to 50% (Fig. 3C). MnO2 is exchange split only at the surface, with a magnetic moment that is orders of magnitude smaller than the thicker Co electrode. Furthermore, the magnetization in MnO2 is limited to the surface with a negligible magnetocrystalline anisotropy, so no stray fields are expected.

Once the light is removed and the charged device is in a floating state, the junction behaves as a leaky capacitor where the accumulated charge, stabilized by the interfacial dipole, moves into the oxide electrode in a time scale dependent on the capacitance of the device and the spin polarization of the trapped charge: \( \tau = C/G \), with \( C \) (G) the spin-dependent capacitance (conductance) of the interface. Charge diffusion to the cobalt electrode may be possible, but electrons would need to hop across several tens of C60 layers and, in some samples, tunnel through an Al2O3 barrier to reach the metal contact. The discharge time \( \tau \) is also dependent on the magnetic structure. When the Co electrode is disordered (e.g., at the in-plane coercive field), charge drains more efficiently. This leads to a 20 to 30% faster voltage drop than when the electrode magnetization is uniform (saturated in plane) (see Fig. 3, D and E).

The polarization of the trapped charge is coupled to the magnetization of the cobalt electrode. Applying increasingly higher OOP fields and measuring at remanence lead to domain formation and demagnetization. The disordered stray fields and changes in magnetization cause the charge traps to vacate, and the LUMO* peak shifts toward the pristine LUMO (Fig. 4A). This LUMO* displacement can be correlated with changes in the discharge time after a junction is optically charged. At remanence after an OOP field, the interface is partly depolarized and \( \tau \) drops by ~40% (Fig. 4B). The change in \( \tau \) is similar to the one seen at the in-plane coercive field, since both maximize the magnetic disorder by bringing the magnetization to zero.

Minority spins at the interface layer, C60(1st), are localized. They cannot move to the electrode unless they undergo spin flip, as there are no minority states available at the Fermi level of the MnOx interface for minority spin electrons to tunnel into. In a charged device, the zero-bias conductance can be approximated by Fermi’s golden rule (40)

\[
G = \sum_{\sigma_0} G^{\sigma_0}(E_F) = \frac{2\pi e^2}{\hbar} \sum_{\sigma_0} T_{21}^{\sigma_0} \rho_{21}^{\sigma_0}(E_F) \rho_{11}^{\sigma_0}(E_F)
\]
Where $G^{\sigma^0}(E_F)$ is the spin-dependent conductance, $T^{\sigma^0}$ is the transmission matrix element for an electron with spin $\sigma$ from C$_{60}$ tunneling to the spin $\sigma'$ band in the MnO$_x$ interface, and $\rho^\sigma(E_F)$ $\rho^\sigma(E_F)$ is the spin split DOS in the initial C$_{60}$ (interface) state. The tunneling probability depends on the projection of the trapped spin at the initial C$_{60}$ layer onto the quantization axis of the final layer. If $\sigma$ and $\sigma'$ are quantized in the same axis, due to spin conservation, then $G^{\sigma^0} = G^{\sigma^0^0} = 0$. Since there are no available states at the interface minority band (e.g., $\sigma^0$, $G^{\sigma^0} = G^{\sigma^0^0} = 0$). However, there are available states for majority electrons, so $G = G^{\sigma^0}$ is changed. When Co is disordered, stray fields with different orientations are generated, and the quantization axis $\sigma$ and $\sigma'$ are not well defined nor parallel across the device, leading to $G \neq 0$ for both orientations (Fig. 4C).

To confirm the presence of localized magnetic ordering due to optical or electrical charging, low-energy muon spin rotation (LE-$\mu$SR) was used. In LE-$\mu$SR, a beam of almost fully polarized positive muons ($\mu^+$) is accelerated at kilo-electron volt energies to be implanted 10 to 100 nm into a sample, providing a highly sensitive probe of the local magnetization (41, 42). Muon acceleration voltages are applied at the moderator, away from the sample, to avoid charging effects. A sample with the structure Co(20)/Al$_2$O$_3$(2)/C$_{60}$(50)/MnO$_x$(5)/C$_{60}$(50)/Cu(15) is charged with the same 0.2 V potential used in NEXAFS (Fig. 5A). Measurements are taken at 250 K, where molecules rotate on timescales (~ps) much faster than the muon decay (~µs). It is then possible to detect the precession in zero magnetic field (ZF) assigned to charged C$_{60}^-$ (11, 29). This state is formed in proximity with metals or when the C$_{60}$ layer is charged, leading to lower cage symmetry and an anisotropic hyperfine coupling of the endohedral muonium state ($\mu^+@C_{60}^-$), with a precession frequency of 0.2 to 1.5 MHz—similar to that observed in ellipsoidal C$_{70}$ (43-45). A zero frequency shows the absence of C$_{60}^-$ away from cobalt (8 to 10 keV) in the ground or biased states. As in NEXAFS, the $\mu$SR signal is unchanged during an applied voltage, but the $\mu^+@C_{60}^-$ frequency, depolarization, and asymmetry (oscillation amplitude) close to the MnO$_x$ interface (10 to 12 keV) are increased in a charged, floating state—all indicative of local magnetism. We attribute the changes to Zeeman splitting of the anisotropic hyperfine levels for $\mu^+@C_{60}^-$ in the magnetic field generated by the trapped polarized charge (Fig. 5, B and C).

A second sample with the structure Ta(5)/Co(20)/Ta(5)/MnO$_x$(10)/C$_{60}$(100)/Cu(5)/Au(15) is photovoltaic. A blue laser is used to generate a photocurrent of 125 µA and charge the interface without a bias (Fig. 5D). The cobalt electrode is close to the active MnO$_x$/C$_{60}$ interface but spin decoupled via a tantalum layer. Measurements in ZF show again an increase in the $\mu^+@C_{60}^-$ frequency during (no bias to discharge the states during the measurement) and after light irradiation (Fig. 5E). The direct current (DC) local magnetic susceptibility is calculated from the diamagnetic response in the muon precession frequency during an applied transverse field of 300 G. The susceptibility increases during and after light irradiation, but only for the energy probing the interface, and reverses to the normal value upon grounding (Fig. 5F and figs. S12 to S15) (39). No light irradiation effect is observed in LE-$\mu$SR measurements of samples without an MnO$_x$ interface.

**CONCLUSION**

The combination of stray fields, spin-polarized interfacial dipole formation, and interface-limited transport observed in MnO$_x$/C$_{60}$ provides a mechanism for spin-dependent charge trapping via an electric bias or light irradiation. The available states and discharge period...
can be controlled via magnetic fields and remain stable at room temperature for macroscopic timescales, leading to optically and/or electrically generated local magnetism. This effect opens new paths of research for electro-optic manipulation of spin information and the development of spin capacitors.

MATERIALS AND METHODS

Junctions were fabricated in a combination sputtering/evaporation chamber using shadow masks to create a vertical junction with a crossed electrode configuration. Metal electrodes were deposited using DC magnetron sputtering in an Ar atmosphere at a pressure of ~2 × 10⁻⁵ mbar, while the molecular layer was thermally evaporated without breaking vacuum at a pressure of 10⁻⁸ mbar. MnO₂ was deposited via sputtering deposition from a 99% pure Mn target and oxidized in an oxygen/argon atmosphere at a 5:1 ratio. For photo-oxidation, the manganese electrode was then plasma oxidized in an argon atmosphere. The manganese electrode was then plasma oxidized in an oxygen/argon atmosphere at a 5:1 ratio. For photo-oxidation, the manganese electrode was then plasma oxidized in an oxygen/argon atmosphere at a 5:1 ratio. For photo-oxidation, the manganese electrode was then plasma oxidized in an oxygen/argon atmosphere at a 5:1 ratio.

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