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Studies of spin related processes in fullerene C₆₀ devices

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We have investigated spin related processes in fullerene C₆₀ devices using a several experimental techniques, which include magnetic field effect of photocurrent and electroluminescence in C₆₀-based diodes; spin polarized carrier injection in C₆₀-based spin-valves; and pure spin current generation in NiFe/C₆₀/Pt trilayer devices. We found that the ‘curvature-related spin orbit coupling’ in C₆₀ plays a dominant role in the obtained spin-related phenomena. The measured magneto-photocurrent and magneto-electroluminescence responses in C₆₀ diodes are dominated by the difference in the *g*-values of hole and electron polarons in the fullerene molecules. We also obtained giant magneto-resistance of ~10% at 10 K in C₆₀ spin-valve devices, where spin polarized holes are injected into the C₆₀ interlayer. In addition, using the technique of spin-pumping in NiFe/C₆₀/Pt trilayer devices with various C₆₀ interlayer thicknesses we determined the spin diffusion length in C₆₀ films to be 13 ± 2 nm at room temperature.

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Introduction

Organic semiconductors (OSEC) have been widely studied over four decades since they show potential applications in optoelectronic devices such as organic light emitting diodes (OLED) [1], organic photovoltaic solar cells [2] and organic field-effect transistors [3]. Specifically, OLED have greatly advanced the display technology in industrial applications. In addition, OSEC have also become popular in the field of spintronics [4] due to their inherent long spin relaxation time compared with that in inorganic semiconductors. The small spin relaxation rates originate from the weak spin orbit coupling (SOC) and hyperfine interaction (HFI) in OSEC, because of the light atoms in their building blocks such as carbon and hydrogen, where the π -electrons play a dominant role in determining the electrical- and spin-related properties of the charge and neutral excitations.

Magneto-resistance in organic diodes, so called organic magneto-resistance (or OMAR), has been observed in various OSEC-based devices [5-8]. OMAR has been traditionally explained by invoking the SOC, which is an interaction that originates from nuclear charge and electron spin via their orbital motion, and hyperfine interaction (HFI) that is a more direct interaction between the nuclear and electron spins [9, 10]. These interactions dominate the inter-conversion between singlet and triplet polaron pair excitations, which is modulated when an external magnetic field is applied to the device [11, 12]. This has been manifested in magneto-conductivity, magneto-photoconductivity and magneto-electroluminescence responses in various organic optoelectronic devices [13].

In addition to the magnetic field effect in organic diodes, where the electrodes are non-magnetic, giant magneto-resistance (GMR) has been also obtained in $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ (LSMO)/OSEC/Co spin-valve devices [4, 14, 15], where the electrodes are ferromagnets (FM). The GMR response originates from a field induced change in the spin scattering rate between the two FM electrodes causing small (large) device resistance when the magnetizations of the two FM electrodes have parallel (antiparallel) configuration. In such devices the OSEC interlayer has been used for spin polarized carriers transport between the two FM electrodes, because of their relatively small spin-lattice relaxation rate. However the spin injection process is limited by the conductivity mismatch problem between the FM electrodes and the OSEC interlayer, and thus the ability to inject spin aligned carriers into the OSEC interlayer is crucially dependent on the FM/OSEC

spinterface states [16-18]. In contrast, pure spin current without the need of charge carrier injection has been recently shown to occur at FM/OSEC interface via the process of spin-pumping [19, 20]. In this case magnon excitations that are generated via FM-resonance (FMR), which carry spin-related angular momentum are scattered at the FM/OSEC interface resulting in excess angular momentum delivered to the electrons in the OSEC layer; this is called 'spin pumping' that leads to pure spin current in the OSEC film. The spin current in the OSEC layer may be detected by a Pt overlayer (which has large SOC) deposited onto the OSEC film, using the inverse spin Hall effect (ISHE) that converts spin-current into electrical current [21, 22]. This method may be used to effectively determine the spin diffusion length of the OSEC, if the measurements are repeated in trilayer FM/OSEC/Pt devices with various OSEC thicknesses.

On the occasion of Fred Wudl 50th anniversary of contribution to the field of Organic Optoelectronics we summarize here our recent investigations of spin-related properties in C_{60} devices. *Fullerenes, and especially C_{60} have been one of the molecules that Fred loved to play with.* Fullerene C_{60} is particularly suitable for spintronic applications since it contains ~99% naturally abundant ^{12}C isotope having spinless nuclei, and thus negligible HFI constant. The intrinsic SOC in the C_{60} molecule is ~10 mK [23], so C_{60} is expected to have large spin diffusion length. However some experiments do not agree with this prediction[24, 25]. It has been theoretically found that the SOC strength, ξ is composed of intrinsic, curvature-related and Rashba terms [24, 26, 27]: $\xi = \xi_{in} + \xi_{curv} + \xi_{Rashba}$. Here ξ_{Rashba} is related to the inversion symmetry breaking and is negligible for C_{60} . Therefore the SOC strength in C_{60} is dominated by ξ_{curv} [24]. The spin polarized carrier transport in C_{60} has been even realized at room temperature by choosing suitable FM electrodes [25, 28]. In addition, spin photovoltaic and magnetic tunnel transistor devices based on C_{60} have been recently achieved [29, 30].

In this contribution, spin related effects have been investigated in various C_{60} based devices. We observed substantial magnetic field effect in C_{60} based diodes in spite of the negligible HFI strength in the fullerenes. We also obtained 10% GMR in LSMO/ C_{60} /Co spin valves at 10 K, indicating efficient spin aligned carrier injection at the FM/ C_{60} interface. In addition, we also determined the spin diffusion length in C_{60} films to be 13 ± 2 nm from ISHE measurements in NiFe/ C_{60} /Pt trilayer devices having various C_{60} thicknesses.

Experimental

(i) C₆₀ diodes: The C₆₀ molecular structure is shown in Figure 1(a) inset. To form high quality thin films, the C₆₀ powder (American Dye Source) was thermally evaporated in high vacuum chamber (1×10^{-7} mbar) at a slow evaporation rate of ~ 0.05 nm/sec. The C₆₀ diode was fabricated with the geometry of indium tin oxide (ITO) semitransparent anode, ~ 40 nm spin-cast polyethylenedioxythiophene/ polystyrene sulphonate (PEDOT:PSS) hole transport layer, ~ 200 nm C₆₀ interlayer, that was capped with ~ 100 nm aluminum layer that serves as cathode. The device structure was thus ITO/PEDOT:PSS/C₆₀/Al with an active area of 2×2 mm².

(ii) C₆₀-based spin-valves: The C₆₀ based spin-valve (SV) was fabricated using 15 nm C₆₀ thin film as spacer in between two FM electrodes, namely 20 nm patterned LSMO (bottom electrode, FM1) and 18 nm Co (top electrode, FM2), as shown in Figure 2(a). The device active crossed section area was 200×200 μm^2 . The devices were placed in a cryostat with variable temperature control in between the two poles of an electromagnet with magnetic field up to 250 mT (having ~ 0.01 mT resolution). The FM/C₆₀ interface was characterized by tunneling electron microscopy (TEM) using a JEOL 2800 apparatus, and cross section view scanning electron microscopy (SEM) using a FEI Helios NanoLab 650 set-up. The magnetic hysteresis loops were measured by a home-made Sagnac MOKE with 10 nrad angular resolution [31].

(iii) C₆₀ devices for ISHE measurements: The ISHE device was fabricated with 15 nm Ni₈₀Fe₂₀ (NiFe) film on glass substrate, followed by C₆₀ layer with various thickness, and capped with 7 nm Pt connected with Cu wires to an electrometer for measuring the ISHE current induced by FMR in the NiFe film. The devices are covered with 100 nm SiO₂ protective layer. NiFe, Pt and SiO₂ were deposited by electron beam evaporation at a base pressure of 1×10^{-7} mbar. The microstructure was characterized by cross section view SEM. The microwave (MW) for the ISHE measurements were generated by an Agilent N5173B amplifier working in the frequency range of 9 kHz to 20 GHz. The samples were put on top of MW guide of 250 μm wide transmission line with the radio frequency magnetic field perpendicular to the DC magnetic field. The ISHE voltage generated in the Pt overlayer was detected by phase-sensitive technique in which MW intensity was modulated by a square wave at 17 kHz.

Results and discussion

(i) Magnetic field effect in C₆₀ diodes

We studied the magnetic field effects (MFEs) in the C₆₀ based diode device, which is given by the percentage change of a physical quantity upon the application of a field, B . For example, the magnetoconductivity response, $MC(B) = 100\% \times (I(B) - I(0))/I(0)$, where I denotes the electric current through the device. Figure 1(a) shows the current-voltage (I-V) and electroluminescence-voltage (EL-V) responses of an ITO/PEDOT: PSS/C₆₀/Al diode at room temperature, which are characteristic responses for organic diodes [24]. Figure 1(b) shows the change of current under applied in-plane magnetic field, $MC(B)$ up to $B=200$ mT measured at a constant voltage of 18 V. $MC(B)$ shows a negative response of nearly 2% having HWHM (half width at half maximum), $B_0 \approx 17$ mT, which is much larger than B_0 of $MC(B)$ response based on HFI mechanism in conjugated polymers (of the order of 5 mT) [5]. We therefore infer that the underlying mechanism for the MC response here is not HFI, but the SOC in the C₆₀ film. Since the internal SOC of carbon is small, we attribute the SOC in the C₆₀ films as due to the curvature of the C₆₀ molecule. The π -electrons do not possess any SOC; however the molecular curvature induces hybridization between the π and σ electrons, which leads to enhanced SOC in C₆₀.

As shown in Figure 1(c), the same C₆₀ device was illuminated with a 405 nm diode laser, and the photocurrent at zero bias was measured as a function of the applied B field to obtain the magneto-photocurrent, $MPC(B)$ response. We observed that the $MPC(B)$ response increases and its HWHM decreases with increasing laser power, which could be explained by the defect generation within the C₆₀ film upon irradiation[32]. We also observed electroluminescence (EL) from the same C₆₀ device when it was operated at a high positive bias voltage. We therefore measure the EL intensity as a function of B field to obtain the magneto-EL response, $MEL(B)$, as shown in Figure 1(d). It is worth mentioning that the MEL response has reversed polarity compared to that of MPC. This shows that the same process that increases the density of singlet excitons with B and thus leads to increase EL intensity and positive MEL; at the same time it decreases the density of photogenerated carriers that leads to a decrease in photocurrent and negative MPC.

In general, the HFI plays an important role in magnetic field effect in OSEC devices; however this is not the case for C_{60} since it has negligible nuclei spin. Moreover, all $MFE(B)$ responses in the C_{60} devices are too broad to be explained based on the HFI mechanism (in which the $MFE(B)$ width is typically ~ 5 mT). We thus attribute the MFE here to the difference, Δg between the g -factors of the hole- and electron-polarons for the C_{60} molecules, the so called “ Δg mechanism” [33, 34]. In this process the spin of the hole- and electron-polarons in the induced spin $\frac{1}{2}$ polaron-pair precesses around the field B at different rates, which results in a spin-mixing between singlet and triplet polaron pairs. We recall that the electron and hole g -factors in C_{60} , obtained using light induced electron spin resonance and doping measurements, respectively, are $g_e = 1.9992$ for the electron-polaron and $g_h = 2.0021$ for the hole-polaron [33, 35, 36]. Thus, under these conditions Δg is determined to be 3×10^{-3} for the C_{60} film. The HWHM, B_0 of the $MFE(B)$ response in the “ Δg model” is given by [28]:

$$B_0 = \frac{\hbar}{2\mu_B \Delta g \tau} \quad (1)$$

where τ is the polaron spin coherence time, and μ_B is the Bohr magneton. Using $B_0 = 17$ mT and $\Delta g = 3 \times 10^{-3}$ in Eq.(1) we estimate $\tau \sim 110$ ns. This is in good agreement with other measurements of τ in C_{60} films using various coherent ODMR measuring techniques [37, 38].

(ii) GMR in C_{60} spin valves

Spin polarized carriers' injection into and transport through C_{60} interlayer is realized in C_{60} based SV, as shown in Fig. 2. Figure 2(a) shows schematics and microstructure of the SV device. We note that the C_{60}/Co interface is flat and very sharp. We may exclude leakage known to exist in organic SV devices based on the following TEM image. Figure 2(b) shows a high resolution TEM image of C_{60}/Co interface. It is clearly seen that the inter diffusion of Co clusters into the C_{60} film is ~ 2 nm, if at all, and that the Co film is polycrystalline. The cross section view SEM image of the organic SV structure is also shown in Fig. S1. The energy dispersive spectroscopy of TEM (see Fig. S2) confirms that there are no inter diffusion clusters from the two FM electrodes. Figure 2(c) shows a typical $GMR(B)$ response of the device for a bias voltage of 100 mV at 10 K. 15 nm C_{60} is sandwiched between two FM, namely LSMO with coercive field, $B_1 = 5$ mT and Co having coercive field $B_2 = 50$ mT at 10 K. Since the two FM have different coercive

fields, it is possible to switch the relative magnetization configuration of the FM electrodes between parallel and antiparallel upon sweeping the magnetic field, as seen in Fig. 2(b) insets. The corresponding magnetic hysteresis loop of the two FM electrodes in the device was characterized by MOKE using our extremely sensitive Sagnac interferometer[31], as seen in Fig. 2(d). Here GMR(*B*) response is defined as $GMR(B)=[R(B)-R(P)]/R(P)$, where *R*(*P*) is the device resistance with parallel magnetization configuration of the two FM electrode. The maximum GMR value, GMR_{max} may be described by the Julliere model:

$$\frac{\Delta R}{R} max = \frac{2P_1P_2e^{-d/\lambda_s}}{1+P_1P_2e^{-d/\lambda_s}} \quad (2)$$

[39], where P_1 and P_2 are the spin polarization of the FM electrodes, and λ_s is the spin diffusion length in the C_{60} film. We mention in passing that GMR_{max} is strongly dependent on the spin injection properties at the FM/ C_{60} interface, which is sensitive to the device fabrication processes. Figure 2(c) shows the bias voltage dependence of GMR_{max} at 10 K. GMR_{max} decreases with increasing the applied voltage. This may be related to the Fermi energy shift with the bias voltage, and consequent change of the effective spin polarizations of the LSMO and Co electrodes. The observed asymmetry of GMR_{max} with *V* is widely reported in the literature[4, 40]. Figure 2(d) shows the temperature dependence of GMR_{max} , which decreases with increasing temperature, *T* and vanishes at $T \approx 250$ K. The GMR_{max} decrease with *T* is mainly due to the temperature dependence of the LSMO spin polarization, since its Curie phase transition temperature is below 300 K. We recall that the interaction between the organic molecules and FM atoms at the molecule/FM interface leads to the formation of chemical bonds [41-44], known as spinterface[16]. Such molecules may modify the magnetic properties of the FM electrodes [41, 45]. In addition the C_{60} molecules may also be spin-polarized by the proximity effect of FM electrodes [43, 46].

(iii) Spin pumping into C_{60} films

Figure 3 describes the detection of pure spin current in C_{60} film generated by the process of spin pumping. Figure 3(a) shows the schematics of the spin pumping process, spin transport through the C_{60} interlayer, and spin detection in the Pt overlayer in the NiFe/ C_{60} /Pt trilayer device. The C_{60} /Pt interface in the trilayer structure is characterized by cross section view SEM (see Fig. 3(a)), which shows a very clear and sharp interface. The spin current in C_{60} is induced at the

NiFe/C₆₀ interface by excess magnons due to the ferromagnetic resonance of the NiFe. The spin current in the C₆₀ film diffuses towards the other interface and reaches the C₆₀/Pt interface while substantially attenuated. The C₆₀ spin current, in turn induces a spin current into the Pt overlayer, which is converted into electric current by the ISHE[19]. The C₆₀ spin current that arrives at the C₆₀/Pt interface is proportional to e^{-d/λ_s} , where d is the C₆₀ film thickness. We note that by using this pure spin current pumping method, we can avoid the resistance mismatch and spinterface problems in SV devices. The upper panel of Fig. 3(b) shows the derivative of the MW absorption in the NiFe substrate under ferromagnetic resonance at room temperature. Consequently, an ISHE voltage is obtained in the Pt overlayer at the corresponding magnetic field, as shown in the lower panel of Fig. 3(b). Figure 3(c) shows the ISHE signal obtained in various NiFe/C₆₀/Pt of different C₆₀ interlayer thicknesses. The sign changes of the ISHE voltage upon changing the magnetic field direction is a proof that we deal with ISHE and not due to several known artifacts, which is consistent with the ISHE theory [47]. Figure 3(d) shows the ISHE signal decay with increasing C₆₀ thickness, which can be well fitted by the relation $V_{\text{ISHE}} \propto e^{-d/\lambda_s}$. From the fit to the obtained data we estimate the spin diffusion length of C₆₀ at room temperature to be $\lambda_s = 13 \pm 2$ nm.

Conclusions

In summary, we have studied the spin-mixing mechanism of spin $\frac{1}{2}$ polaron pairs, spin polarized carrier transport and pure spin current transport in a series of C₆₀ thin-film devices. Although the HFI in C₆₀ films is miniature, SOC still exists due to the ‘curvature induced hybridization’ between the π and σ electrons of the spherical molecule, and is strong enough to influence the spin-related effects in C₆₀ films. The magnetic field responses in C₆₀ diodes with non-magnetic electrodes such as MPC, MC and MEL are interpreted as due to the “ Δg mechanism” between the electron and hole in the C₆₀ film. From the HWHM of the MFE(B) responses we obtained the spin lifetime of polaron pair ~ 110 ns. In addition we obtained GMR of $\sim 10\%$ in C₆₀ based SV devices at low temperature. The bias voltage and temperature dependences of the measured GMR are similar to that in other organic SVs. The generation of pure spin current in C₆₀ films has been realized based on the spin pumping effect; from its C₆₀ interlayer thickness dependence we obtained the spin diffusion length in C₆₀ films to be $\lambda_s = 13 \pm 2$ nm at room temperature.

These findings imply the great potentials of fullerene-based materials in studying spin-related phenomena and fabricating novel effective organic spintronic devices.

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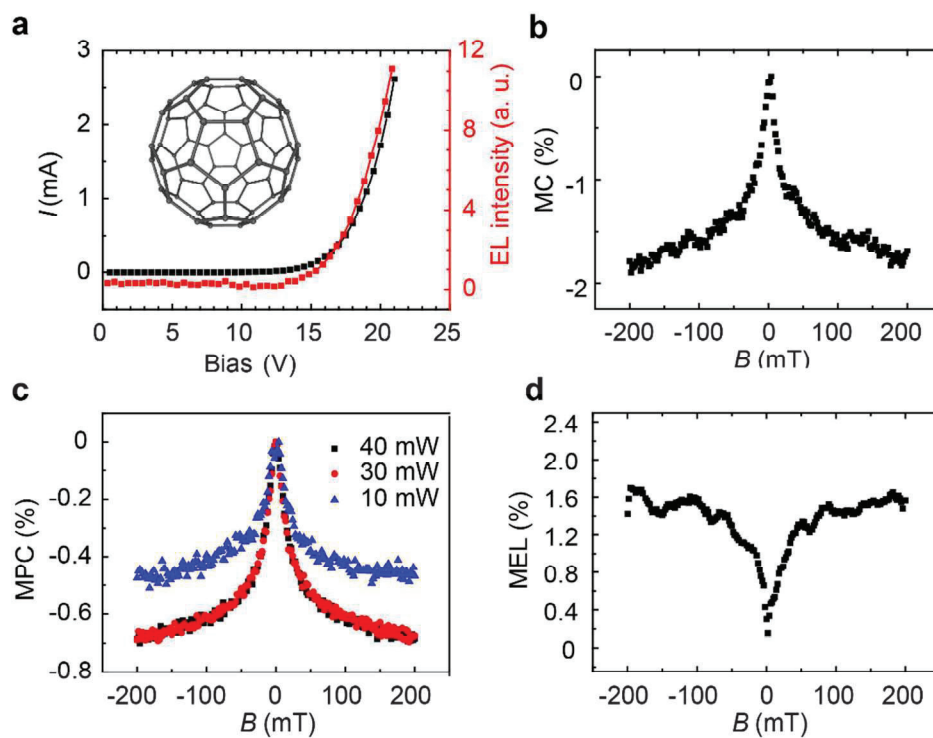


Figure 1. Magnetic field effects in the C_{60} based device. a, I-V (black) and EL-V (red) device responses at forward bias. Inset: molecular structure of C_{60} . b, $MC(B)$ response measured at applied bias voltage of 18 V at room temperature. c, $MPC(B)$ response under illumination of 405 nm laser at different laser powers, as given. d, $MEL(B)$ response from the same device measured at positive bias voltage of 20 V.

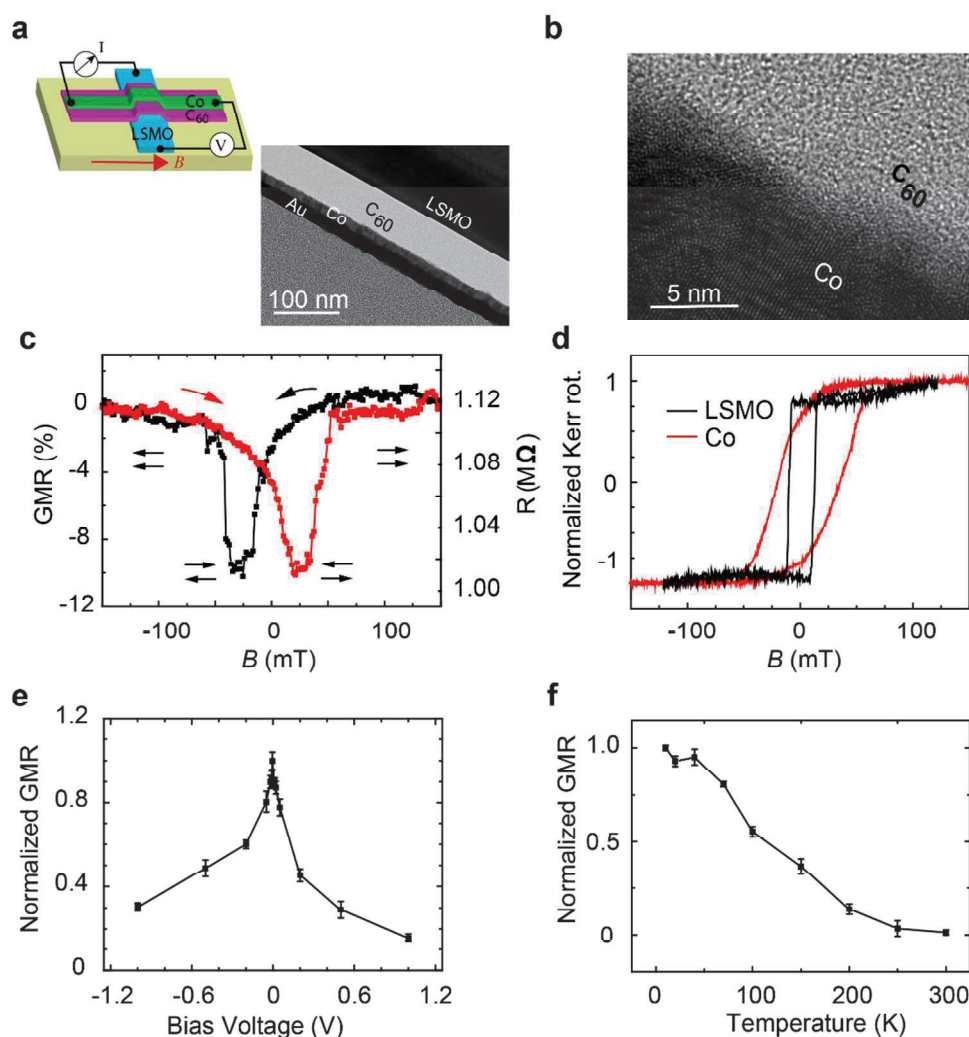


Figure 2. GMR in C_{60} based SV devices. a, Schematics of the SV device structure and a typical low resolution TEM image. Here the C_{60} film is sandwiched between two ferromagnet electrodes, namely LSMO and Co. The current change under a fixed voltage is recorded when sweeping the magnetic field. b, High resolution TEM image of the C_{60} /Co interface. c, GMR(B) response in LSMO (20 nm)/ C_{60} (15 nm)/Co (30 nm) SV measured at an applied bias voltage of 100 mV. The maximum GMR, GMR_{max} value is $\sim 10\%$. d, the magnetic hysteresis loops of the spin valve device measured by MOKE using a Sagnac interferometer. e and f, bias voltage and temperature dependencies of the measured GMR_{max} .

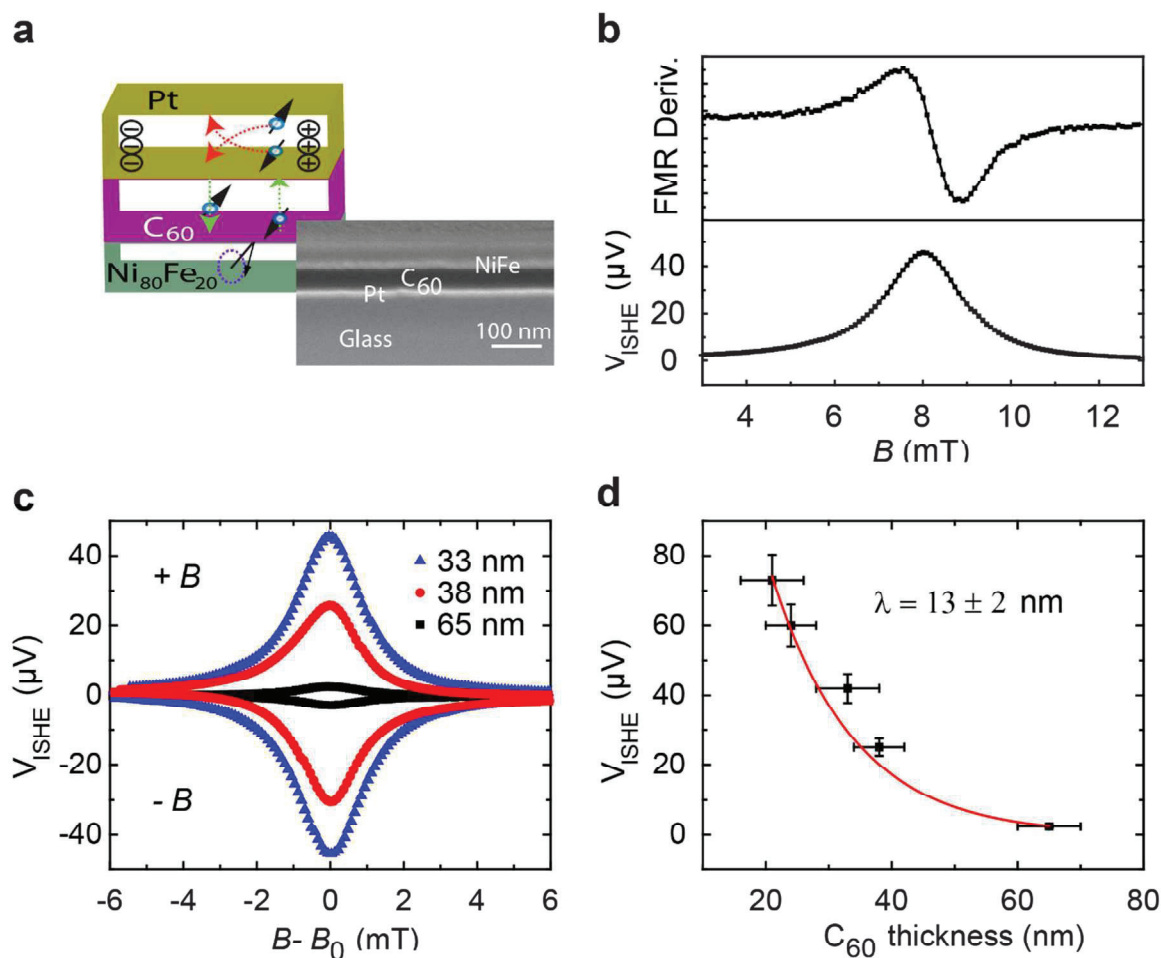


Figure 3. Pure spin current generation in and transport through C_{60} film based on the spin-pumping effect. a, schematics and microstructure of the device. The microstructure is characterized by cross section view of SEM. The $NiFe$ FM substrate operates at magnetic resonance condition that generates excess magnon excitations. Spin angular momentum carried by the magnons is transferred to the C_{60} electrons at the $NiFe/C_{60}$ interface via the spin-pumping effect. The induced spin current in the C_{60} film diffuses away from the $NiFe/C_{60}$ interface and reaches the C_{60}/Pt interface. The induced spin current in the Pt overlayer is converted into electrical current via the ISHE. The magnetization, spin current and electric current directions are all perpendicular to each other. b, derivative of the microwave absorption in the $NiFe$ film at FMR condition (upper panel) and corresponding ISHE signal obtained in the Pt overlayer (lower panel) at room temperature. c, ISHE signals obtained in Pt layer of $NiFe/C_{60}/Pt$ trilayer devices having various C_{60} interlayer thicknesses. The sign change of the ISHE voltage is due to the reversal of the magnetic field direction. B_0 is resonant field. d, C_{60} interlayer thickness

dependence of the ISHE voltage measured from the Pt overlayer. The red line is an exponential fit, from which we obtain the spin diffusion length in C_{60} as given.