



Giant Spin Seebeck Effect through an Interface Organic Semiconductor

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New concepts

An organic semiconductor such as C_{60} buckminster fullerene is a promising candidate material for organic spintronic devices due to its low spin-orbit coupling that essentially results in weak spin scattering and consequently a large spin diffusion length. By exploiting these superior properties of C_{60} , we have tackled one of the most challenging problems (e.g. conductivity mismatch and uncoupled interface effects) in generation and transmission of large pure spin currents in ferromagnetic insulator/non-magnetic, large spin-orbit interaction metal systems like $Y_3Fe_5O_{12}$ (YIG)/Pt. We demonstrate, for the first time, through spin Seebeck effect (SSE) experiments and density functional theory (DFT) calculations that the presence of C_{60} reduces significantly the conductivity mismatch between YIG and Pt and the surface perpendicular magnetic anisotropy of YIG, giving rise to enhanced spin mixing conductance across YIG/ C_{60} /Pt interfaces. We also establish a relationship between the spin diffusion length of the intermediate layer (C_{60}) and the SSE voltage in this type of heterostructure. Our study provides a new pathway for designing novel hybrid materials with prospective applications in spin caloritronics and other multifunctional devices.

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Giant Spin Seebeck Effect through an Interface Organic Semiconductor

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Interfacing an organic semiconductor C₆₀ with a non-magnetic metallic thin film (Cu or Pt) has created a novel heterostructure that is ferromagnetic at ambient temperature, while its interface with a magnetic metal (Fe or Co) can tune the anisotropic magnetic surface property of the material. Here, we demonstrate that sandwiching C₆₀ in between a magnetic insulator (Y₃Fe₅O₁₂: YIG) and a non-magnetic, strong spin-orbit metal (Pt) promotes highly efficient spin current transport via the thermally driven spin Seebeck effect (SSE). Experiments and first principles calculations consistently show that the presence of C₆₀ reduces significantly the conductivity mismatch between YIG and Pt and the surface perpendicular magnetic anisotropy of YIG, giving rise to enhanced spin mixing conductance across YIG/C₆₀/Pt interfaces. As a result, a 600% increase in the SSE voltage (V_{LSE}) has been realized in YIG/C₆₀/Pt relative to YIG/Pt. Temperature-dependent SSE voltage measurements on YIG/C₆₀/Pt with varying C₆₀ layer thicknesses also show an exponential increase in V_{LSE} at low temperatures below 200 K, resembling the temperature evolution of spin diffusion length of C₆₀. Our study emphasizes the important roles of the magnetic anisotropy and the spin diffusion length of the intermediate layer in the SSE in YIG/C₆₀/Pt structures, providing a new pathway for developing novel spin-caloric materials.

1. Introduction

Generating pure spin currents has been the main challenge for realizing highly efficient spintronics devices.¹ Notable effects under study for attaining pure spin currents are the spin Hall effect (SHE)², spin pumping mechanism^{3,4}, and the spin Seebeck effect (SSE).^{5,6} In the last two approaches, a pure spin current is generated in a ferromagnetic (FM) material (which could be a metal⁷, insulator⁸, or semiconductor⁹) and converted into a voltage drop via the inverse

spin Hall effect (ISHE) in a nonmagnetic metal (NM) possessing strong spin-orbit coupling. In case of the SSE, the spin current J_s can be expressed as¹⁰

$$J_s = \frac{G}{2\pi M_s V_a} \gamma \hbar K_b \Delta T, \quad (1)$$

where G is the spin mixing conductance, γ is the gyromagnetic ratio, V_a is the magnetic coherence volume, M_s is the saturation magnetization, and ΔT is the temperature difference between magnons in FM and electrons in NM. One of the key parameters essential for an efficient spin transport across a FM/NM interface is having a large spin mixing conductance, which directly correlates with a large spin current, as evident from Eq. (1).¹⁰ According to Eq. (1), increasing G is essential to transport large spin currents from FM to NM.

Since the first observation of SSE in the ferromagnetic insulator Y₃Fe₅O₂ (YIG) in 2010,⁸ this material has become one of the most intensively studied systems for fundamental understanding of the underlying spin transport and for prospective spin caloritronic applications, among others.^{5,6} Significant efforts have been devoted towards improving the value of G and hence the SSE voltage by utilizing YIG/Pt interfaces and adding various thin intermediate layers, such as Cu, NiO, CoO, Fe₇₀Cu₃₀, NiFe, or Py.¹¹⁻¹⁵ Inserting a non-magnetic layer of Cu, for example, between YIG and Pt has been reported to decrease the SSE signal¹⁴, while the addition of an ultrathin magnetic layer of Fe₇₀Cu₃₀¹⁴ or NiFe¹⁵ between YIG and Pt has increased the magnetic moment density or G at their interface, leading to an overall improvement in the SSE voltage. Recently, Lin *et al.* reported a significant enhancement of the SSE in YIG/M/Pt (M = NiO or CoO) heterostructures,¹² demonstrating the important role played by an additional antiferromagnetic layer on the spin current transport. Despite the enhancement of SSE reported in these heterostructures, the responsible underlying mechanisms associated with the role of the intermediate layer on the SSE have remained an open question.¹⁰⁻¹⁵

It is generally accepted that spin transport through a material is limited by its spin diffusion length λ . While YIG has a large λ (~10 μ m), a small λ value of Pt (~2 nm) has been reported.¹⁶ Consequently, undesired effects, such as large surface roughness of

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YIG¹⁷ and/or large perpendicular surface magnetic anisotropy of YIG¹⁸ causing strong spin scattering, could suppress considerably the spin current injection into the Pt layer. The large conductivity mismatch between YIG and Pt could also decrease considerably the efficient spin transport in YIG/Pt.¹⁹ It is therefore desirable to seek an intermediate material that can reduce both the perpendicular surface magnetic anisotropy of YIG and the conductivity mismatch between the YIG and Pt layers.

In this regard, an organic semiconductor (OSC) such as C₆₀ buckyballs can be considered as a promising candidate material due to its low spin-orbit coupling that essentially results in weak spin scattering and consequently a large spin diffusion length (λ can be of the order of several hundred nanometers).^{20,21} Additionally, the C₆₀ buckyballs are semiconducting in nature²², thus when sandwiched between YIG and Pt layers, the conductivity mismatch between them is likely to be reduced. Recent studies have also revealed that C₆₀ hybridizes strongly with metallic substrates, which leads to inducing ferromagnetic order at the surface layer of a non-magnetic metal, such as Cu or Pt²³, or tuning the surface magnetism (e.g. surface magnetic anisotropy) of a magnetic metal, such as Fe or Co.²⁴ These findings lead us to propose a new approach for improving the SSE in ferromagnetic insulator/metal systems such as YIG/Pt by adding a thin intermediate layer of an organic semiconductor such as C₆₀ and forming a novel heterostructure of YIG/C₆₀/Pt, as shown in Fig. 1. In this Letter, we synthesize YIG/C₆₀/Pt systems containing buckyball layers of various thicknesses and report the first comprehensive experimental demonstration of thermally generated pure spin currents in the systems through the longitudinal SSE (LSSE). Our experiments show that the spin current in the YIG/C₆₀/Pt heterostructures is significantly enhanced as compared to YIG/Pt structures. This enhancement can be as large as 600% and it is dependent on temperature and the thickness of the C₆₀ layer. We demonstrate that the long spin diffusion length of C₆₀ has a much pronounced positive impact on the SSE signal. The exponential temperature dependence of both the SSE voltage and λ suggests that λ scales with the SSE voltage in magnitude. Our first principles calculations based on density functional theory (DFT) corroborate the experimental measurements and provide further insight into the role of C₆₀ on the transport and magnetic properties of the YIG/C₆₀/Pt heterostructure.

2. Experiments

Single crystal YIG was purchased from Crystal Systems Corporation, Hokuto, Yamanashi, Japan, which was grown using Floating zone method along (111) direction. Various layers of C₆₀ were deposited on top of the YIG surface, using the thermal evaporation method with the evaporation rate of 0.2 Å/s at the base pressure of 2×10^{-7} torr. Figure 1b shows the SEM cross-section and EDX color map image of the 50 nm thick C₆₀ deposited YIG slab. From the SEM image, it can be concluded that the C₆₀ was evenly deposited on the surface of the YIG single crystal slab.

Longitudinal spin Seebeck voltage measurements were performed on a YIG single crystal of dimension 6 mm × 3 mm × 1 mm (length ×

width × thickness). A platinum strip of 6 mm × 1 mm × 15 nm was deposited on YIG using DC sputtering. The sputtering chamber was evacuated to a base pressure of 5×10^{-6} Torr and Argon pressure of 7 mT during the deposition. DC current and voltage used for deposition were 50 mA and ~350 V, respectively. The schematic of the LSSE measurement set-up is shown in Fig. 1a. For LSSE measurements YIG/Pt was sandwiched between two copper plates. A Peltier module was attached to the bottom plate and top plate temperature was controlled through molybdenum screws attached to the cryogenic system. A temperature gradient of approximately 2 K was achieved by applying 3 A current to the Peltier module. K-type thermocouples were used to monitor the temperature of the top and bottom plates. After stepping the system temperature and Peltier module current, measurements were performed after 2 h of stabilization time. The SSE voltage was recorded as the magnetic field was swept between positive and negative saturation of YIG, using a Keithley 2182 Nano voltmeter.

Transverse susceptibility (TS) measurements were performed using a self-resonant tunnel diode oscillator with a resonant frequency of 12 MHz and sensitivity in resolving frequency shift on the order of 10 Hz.^{25,26} The tunnel diode oscillator is integrated with an insert that plugs into a commercial Physical Properties Measurement System (PPMS, Quantum Design), which is used to apply dc magnetic fields (up to ± 7 T) as well as provide the measurement temperature range ($10 \text{ K} < T < 300 \text{ K}$). In the experiment, the sample is placed in an inductive coil, which is part of an ultrastable, self-resonant tunnel-diode oscillator in which a perturbing small RF field ($H_{AC} \approx 10 \text{ Oe}$) is applied perpendicular to the DC field. The coil with the sample is inserted into the PPMS chamber which can be varied the temperature from 10 K to 350 K in an applied field up to 7 T.

Computational Methods

The first principles simulations are performed using the local spin density approximation to the density functional theory (DFT) as implemented in the Quantum ESPRESSO package²⁷. We use ultrasoft pseudopotentials with a kinetic energy cutoff of 320 eV. The exchange-correlation is treated within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation²⁸. For the calculations, we

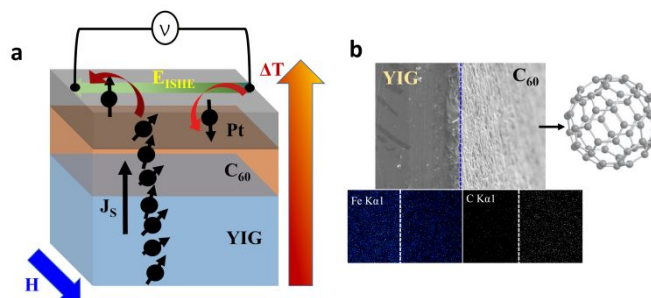


Figure 1 (a) Measurement geometry and spin transport through the YIG/C₆₀/Pt layer. (b) Cross-sectional SEM and EDX color map images of the 50 nm thick C₆₀ deposited YIG slab.

D (Å)	$d_{Fe-C}^{(1)}$ (Å)	$d_{Fe-C}^{(2)}$ (Å)	d_{Pt-C} (Å)	$d_{C60-C60}$ (Å)	$\delta_{Pt}^{(1)}$ (Å)	$\delta_{Pt}^{(2)}$ (Å)	δ_{Fe} (Å)
10.33 (10.31)	2.021 (2.02)	2.25 (2.25)	2.21 (2.198)	4.13 (4.13)	0.44 (0.4)	0.22 (0.18)	0.11 (0.11)

Table 1 Relaxed structural parameters of the Fe/C₆₀/Pt layer shown in Figs 3a and 3b. Specifically, D , $d_{Fe-C}^{(1,2)}$, d_{Pt-C} , $d_{C60-C60}$, $\delta_{Pt}^{(1,2)}$, and δ_{Fe} (in Å) represent the separation between the Fe and Pt layers, the lengths of the covalent bonds formed between the Fe and C atoms, between Pt and C atoms, the distance between the C₆₀ molecules, and the displacements of the Pt and Fe atoms located immediately in the vicinity of the C₆₀ molecule, respectively. The numbers in parenthesis represent the same distances calculated by including the vdW correction.

construct a supercell consisting of equally spaced C₆₀ buckyballs sandwiched between a Fe layer composed of three bcc Fe (001) monolayers and a Pt layer composed of three fcc Pt (001) monolayers. In total the supercell consists of 156 atoms with 48 Pt atoms, 48 Fe atoms and 60 C atoms. The reciprocal space is sampled with a uniform Monkhorst-Pack 4 × 4 × 1 mesh. The outermost Fe and Pt monolayers are kept fixed during the relaxation, and all the other atoms are allowed to relax until the change in energy is less than 10⁻⁵ eV and the forces acting on atoms are less than 0.02 eV/Å. We also included the vdW-D3 dispersion correction²⁹ in the calculations.

3. Results and discussion

Effect of C₆₀ on the bulk and surface magnetic properties of YIG

First, we show how the coating of C₆₀ modifies the bulk and surface magnetic properties of YIG by means of magnetometry and radio-frequency (RF) transverse susceptibility. Figure 2a shows the magnetic hysteresis (M - H) loops taken at 300 K for YIG, YIG/Pt and YIG/C₆₀(5 nm)/Pt structures. All three plots superimposed on each other, indicate that it is not possible to use magnetometry to identify the magnetic difference among these samples. In a recent study, we have demonstrated the excellent capacity of using our RF transverse susceptibility (TS) technique to probe the surface perpendicular magnetic anisotropy (PMA) field and its temperature evolution in YIG, providing the first experimental evidence for a

strong effect of the surface PMA on V_{LSSE} .²⁵ Note that TS uses a self-resonant tunnel diode oscillator with a resonant frequency of ~12 MHz. The sensitivity of 10 Hz has been reached and validated by us over the years as a highly efficient tool for precisely measuring magnetic anisotropy in a wide range of magnetic materials.^{25,26,30-32} In the present study, we have performed detailed TS experiments on YIG, YIG/Pt, and YIG/C₆₀/Pt structures. Figure 2b shows typical TS curves at 200 K for these samples as dc magnetic field was swept from positive saturation to negative saturation. As the field was swept from positive to negative saturation, the first peak corresponds to the bulk magnetocrystalline anisotropy field (H_K) and the second peak corresponds to the surface/interface magnetic anisotropy field (H_{KS}) of the system. The unique TS method of measuring magnetic anisotropy provides the advantage of measuring surface and bulk anisotropy separately. Since SSE is a surface/interface-related phenomenon, we are interested in H_{KS} and its temperature evolution, as it controls surface magnetization and hence LSSE voltage. Figure 2c shows the temperature dependence of H_{KS} for the YIG, YIG/Pt, and YIG/C₆₀/Pt samples. As expected, $H_{KS}(T)$ for YIG shows a peak around 75 K, which has been attributed to the rotation of surface spins away from the perpendicular easy-axis direction.²⁵ It is worth noting in Fig. 2c that while the coating of Pt on the surface of YIG considerably increases H_{KS} in YIG/Pt, as compared to YIG, the coating of C₆₀ on the surface of YIG drastically decreases H_{KS} in YIG/C₆₀/Pt.

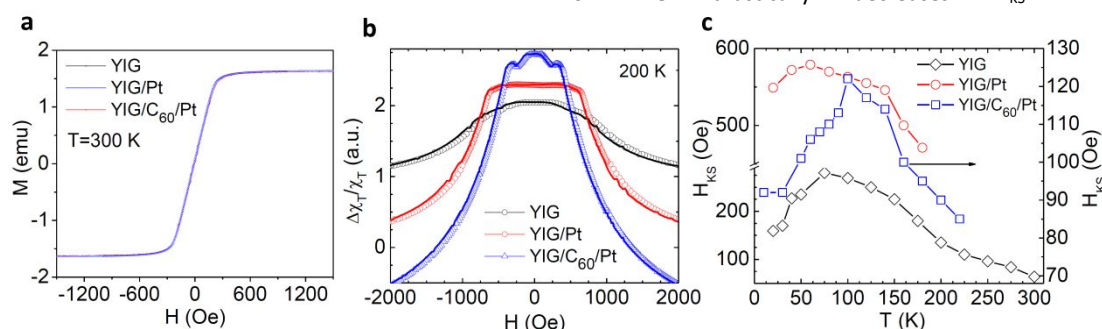


Figure 2 (a) Magnetic hysteresis (M - H) loops taken at 300 K for YIG, YIG/Pt, and YIG/C₆₀/Pt structures; (b) Transverse susceptibility spectra taken at 200 K for YIG, YIG/Pt, and YIG/C₆₀/Pt structures; and (c) Temperature dependence of surface/interface perpendicular magnetic anisotropy field (H_{KS}) for YIG, YIG/Pt, and YIG/C₆₀/Pt structures.

The decrease in H_{KS} in YIG/C₆₀/Pt can be due to the hybridization between the d_z^2 orbital of Fe and p orbitals of C atoms.²⁴ As H_{KS} inversely scales with V_{LSSE} ,²⁵ the decrease in H_{KS} of YIG due to C₆₀

interface is expected to increase V_{LSSE} in YIG/C₆₀/Pt relative to YIG/Pt. To provide an in-depth understanding of the interfacial properties of the YIG/C₆₀/Pt system in regards to the experimental

measurements, we perform first principles simulations based on DFT for the atomic and electronic structure properties of the studied system. Details of the computational approach are given in the Methods section. Due to the limitations imposed by the complexity of the studied composite and the potentially large number of atoms in the supercell, we take advantage of the fact that the majority of the magnetic moment within the YIG unit cell is highly localized to the Fe sites³³, and thus model the YIG layer by a Fe layer. The periodically distributed C₆₀ molecules between Fe and Pt layers, each composed of three monolayers, are shown in Fig. 3a, where some characteristic distances are also denoted. To get a better idea of the atomic bonds of C-Pt and C-Fe, a schematic accentuating the atomic locations directly above and below of the buckyball are shown in Fig. 3b together with some relative displacements with respect to the horizontal planes fixed by the rest of the atoms in the Fe and Pt layers. It is found that, in the relaxed configuration, the C₆₀ molecule is chemisorbed with one hexagonal C face atop of one Pt atom, which gets pushed below the initial layer position by $\delta_{Pt}^{(1)} \approx 0.4$ Å, while the neighboring Pt atoms are pulled above by $\delta_{Pt}^{(2)} \approx 0.2$ Å. The Fe atoms in the immediate vicinity of the C₆₀ cage are also displaced by $\delta_{Fe} \approx 0.1$ Å forming an armchair. The C atoms in the hexagonal face adjacent to the Pt layer form chemical bonds with a length of $d_{Pt-C} \approx 2.2$ Å, while those in the hexagon close to the Fe layer form bonds with inequivalent lengths of $\delta_{Fe-C}^{(1)} \approx 2$ Å and $\delta_{Fe-C}^{(2)} \approx 2.25$ Å,

respectively. The distance between the C₆₀ molecules is $d_{C_{60}-C_{60}} \approx 4.13$ Å and it is larger than the overall separation of 3.13 Å of the buckyball crystal³⁴, which ensures a minimal interaction between adjacent buckyballs. All structural parameters are summarized in Table 1, where results including the effects of the van der Waals interaction via the DFT-D3 approach are also shown. Our calculations indicate that most of the characteristic distances do not change significantly, although D is reduced by 0.01 Å, while $\delta_{Pt}^{(1)}$ and $\delta_{Pt}^{(2)}$ are reduced by 0.04 Å and 0.03 Å, respectively, upon taking the van der Waals dispersion into account.

The calculated average magnetic moments per layer are also shown in Fig. 3b. The C atoms in the hexagonal face close to the Fe layer acquire an antiparallel average magnetic moment of about 0.01 μ_B . The intercalation of the C₆₀ molecule decreases the magnetic moments of the interfacial Fe atoms in the immediate vicinity of the C₆₀ cage to 2.27 μ_B , while it reduces to zero the proximity induced magnetization of the Pt atoms in the first layer near the C₆₀ cage. This suggests that there is a reduction of the interfacial PMA, which is consistent with our measurements of H_{KS} in YIG/C₆₀/Pt, and it is attributed to the hybridization of the Fe d_{z^2} orbitals with C p_z orbitals²⁴. We also calculate the electronic density of states (DOS), where the spin-resolved results are given in Fig. 3c, while the total density of states is shown in Fig. 3d. In addition to DOS for the Pt/C₆₀/Fe, we also present the obtained DOS for the Pt/Fe for comparison.

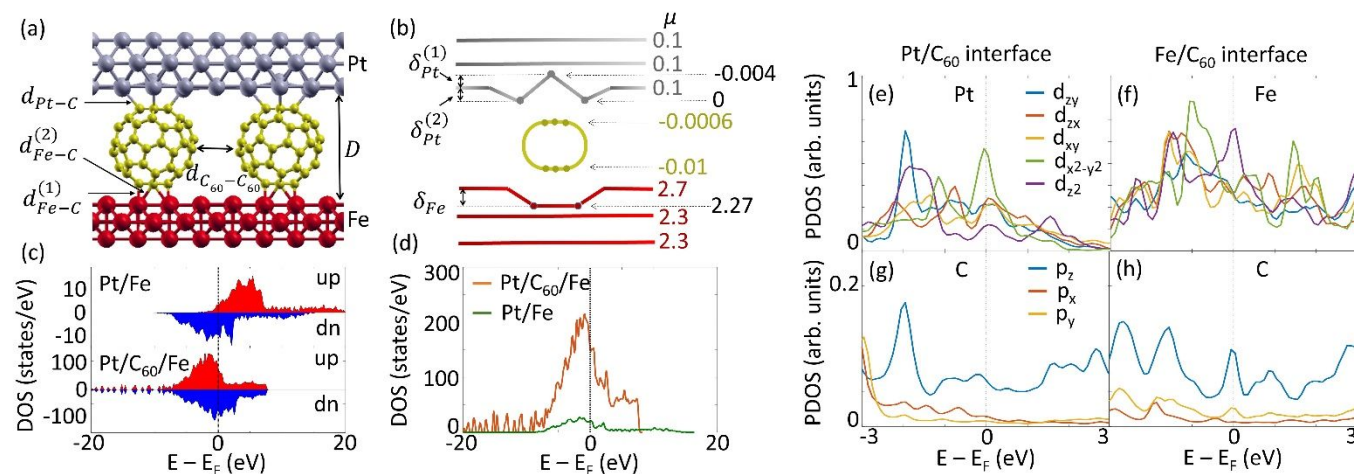


Figure 3 (a) The Pt/C₆₀/Fe heterostructure, where Pt and Fe atoms are indicated with grey and red colors and C atoms are in yellow. Characteristic interatomic distances are also denoted. (b) Schematic representation of the Pt/C₆₀/Fe relaxed structure, showing the buckling (enhanced to help visualization) of the innermost Pt and Fe layers due to the intercalation of the C₆₀ molecules. Some characteristic vertical displacements are also shown. The numbers on the right represent the calculated average magnetic moments, in Bohr magneton, per layer. The considered C layers in are composed of the C hexagons closest to the metallic surfaces. (c) Spin resolved DOS for the Pt and Fe layers, with and without the C₆₀ molecule. (d) Total DOS for the same structures as in (c). (e) PDOS on the d orbitals of Pt and (g) on the p orbitals of C atoms forming the chemical bonds at the Pt/C₆₀ interface. (f) PDOS on the d orbitals of Fe and (h) on the p orbitals of C atoms forming the chemical bonds at the Fe/C₆₀ interface.

The Fe/Pt structure is formed by removing the C₆₀ molecules and allowing the adjacent layers of Pt and Fe to relax and bond. It is interesting to note that while the Pt/Fe system exhibits a spin-polarized DOS near the position of the Fermi level, with the minority spins having the dominant contribution to the transport,

for the Pt/C₆₀/Fe structure both spins contribute almost equally to the DOS at the Fermi level (Fig. 3c). This ultimately leads to a reduction in the conductivity mismatch between the Pt and Fe layers as a result of the C₆₀ interface. This situation is further clarified by the total DOS in Fig. 3d, which shows a significant

enhancement of the conduction states near E_F for the Pt/C₆₀/Fe heterostructure as compared to the Pt/Fe system. In fact, it is found that DOS at E_F for Pt/C₆₀/Fe is about 600% larger than DOS at E_F for Pt/Fe, which further corroborates the giant SSE enhancement in our experiments. Even though the synthesized samples involve layers with different C₆₀ thicknesses, we note that the individual buckyball has an energy gap between its highest occupied molecular orbital and the lowest unoccupied molecular orbital, which is very similar to the semiconducting gaps of a linear chain of C₆₀ molecules³⁵, thus the characteristic DOS behavior is due to the interface effects with the Pt and Fe layers and they are expected to be preserved regardless of the thickness of the C₆₀ layer. Thus the simulated structure as depicted in Fig. 3a is expected to be a good representative of the measured samples.

To bring further insight into the orbital hybridization effects at the interfaces of the C₆₀ molecule with the Pt and Fe layers, we calculate the projected density of states (PDOS) on the relevant atomic species involved in forming the chemical bonds at these interfaces. The results are displayed in Figs. 3 e-h, with Figs. 3e and 3g showing the PDOS on the d orbitals of Pt and on the p orbitals of C atoms at the Pt-C₆₀ interface, and Figs. 3f and 3h showing the PDOS on the d orbitals of Fe and on the p orbitals of C atoms at the Fe-C₆₀ interface, respectively. As apparent from Figs. 3e and 3g, the enhancement of the conductivity at the Pt-C₆₀ interface may be mainly attributed to the hybridization of the $d_{x^2-y^2}$ orbitals of Pt with the p_z orbitals of C, while at the Fe-C₆₀ interface the d_z^2 orbitals of Fe hybridize with the p_z orbitals of C. Therefore, the observed increase in the conduction states near E_F is manifestation of a complex orbital hybridization of the Pt, Fe, and C atoms taking place locally at both interfaces.

Effect of C₆₀ on the LSSE voltage in the YIG/C₆₀/Pt structure

Figures 4a and b show the LSSE voltage (V_{LSSE}) vs. magnetic field (H) curves for YIG/C₆₀/Pt samples with varying C₆₀ thicknesses ($t_{C60} = 0, 5, 10, 30,$ and 50 nm) at two representative temperatures of 140 and 300 K, for a temperature gradient of $\Delta T = 2$ K. Since there is no anomalous Nernst effect in YIG/C₆₀ (Fig. S1, Supplementary Information), the V_{LSSE} signals we have observed in YIG/C₆₀/Pt are dominated by the LSSE. Contribution of the C₆₀/Pt interface to the V_{LSSE} signals is also negligible (Fig. S2, Supplementary Information). It can be seen in Fig. 4 that in the low field region ($H \leq \pm 0.3$ kOe), V_{LSSE} is relatively small (almost zero) and remains almost unchanged with increasing the magnetic field. This low field anomaly has been attributed to the presence of the surface PMA of YIG.^{18,25} It is worth mentioning in the present case that even after the introduction of the C₆₀ layer between the YIG and Pt layers, the anomalous low field $V_{LSSE}(H)$ behavior is still persistent, underlining the same mechanism for LSSE voltage generation in YIG/C₆₀/Pt. Saturated V_{LSSE} has been calculated as the average of positive and negative peak voltages. At 300 K, YIG/Pt with no C₆₀ layer has produced V_{LSSE} of 110 nV (Fig. 4a). When a 5 nm C₆₀ film was introduced between the YIG and Pt interfaces, V_{LSSE} increased to 190 nV. The enhancement of V_{LSSE} due to the C₆₀ intermediate layer becomes more prominent at low temperature. At 140 K, V_{LSSE} increases from 70 to 660 nV with the insertion of the 5 nm C₆₀ thin film (Fig. 4b). As can be summarized in Fig. 4c, when the thickness of C₆₀ is increased from 5 to 50 nm, V_{LSSE} decreases sharply first and then gradually. At 300 K, YIG/C₆₀/Pt samples with $t_{C60} = 10, 30,$ and 50 nm show smaller values of V_{LSSE} as compared to YIG/Pt. At 140 K, however, the opposite trend is observed. For the thickest C₆₀ layer (50 nm), the V_{LSSE} value of YIG/C₆₀/Pt is still greater than that of YIG/Pt.

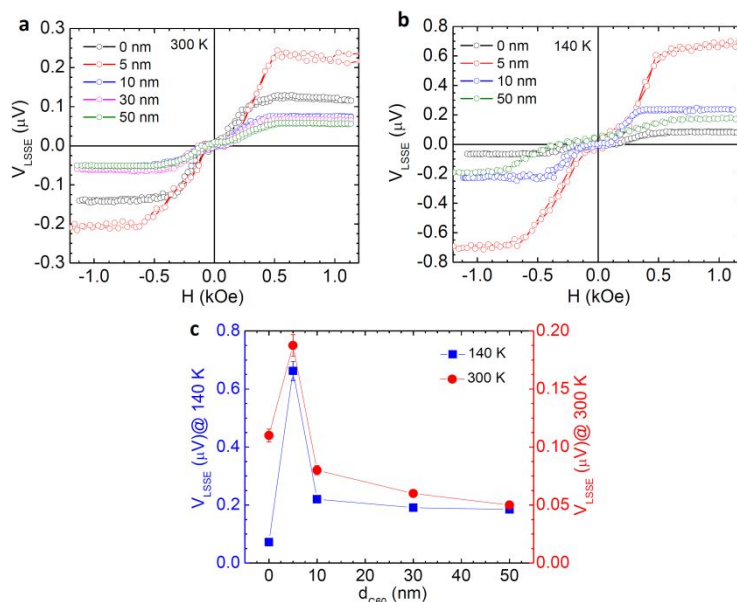


Figure 4 LSSE voltage vs. magnetic field curves taken at (a) 300 K and (b) 140 K for YIG/C₆₀/Pt with different thicknesses of C₆₀. (c) C₆₀ thickness dependence of the LSSE signal at 300 K and 140 K.

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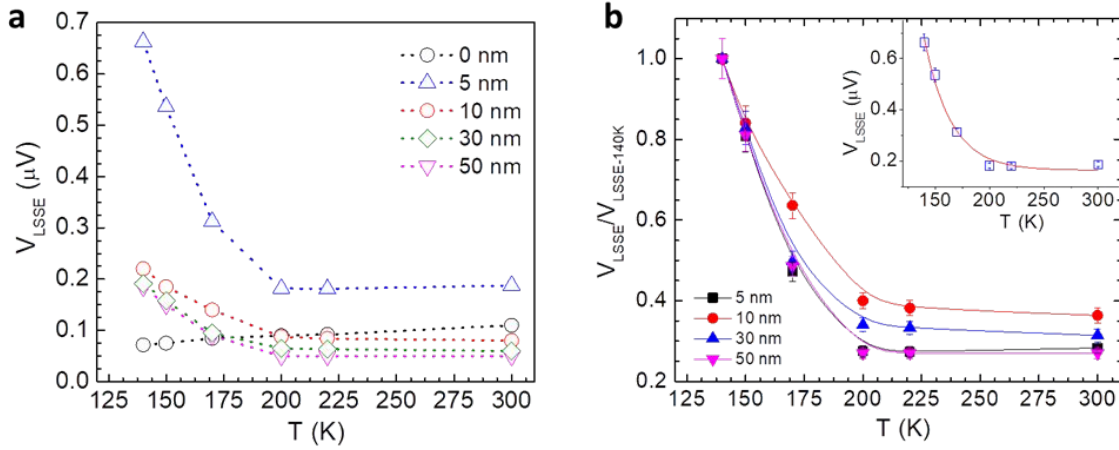


Figure 5 (a) Temperature dependence of LSSE voltage for YIG/ C_{60} /Pt with different thicknesses of C_{60} ; (b) The normalized value of LSSE for different C_{60} thicknesses of YIG/ C_{60} /Pt. Inset of (b) shows the fit for the 5 nm C_{60} thickness. The temperature dependence of spin diffusion length determined from our SSE method and the MR method.³⁶

If we convert the V_{LSSE} values taken at 150 K to LSSE coefficients, we obtain the S_{LSSE} values of $\sim 0.23 \mu\text{V}/\text{cm}$ for YIG/Pt and $\sim 2.2 \mu\text{V}/\text{cm}$ for YIG/ C_{60} (5nm)/Pt.

To elucidate the observed phenomenon, we have studied in detail the temperature evolution of V_{LSSE} in YIG/Pt, YIG/ C_{60} (5 nm)/Pt, YIG/ C_{60} (10 nm)/Pt, YIG/ C_{60} (30 nm)/Pt, and YIG/ C_{60} (50 nm)/Pt. All measurements were performed from 300 to 140 K, and the results are shown in Fig. 5a. It should be recalled that for YIG/Pt (with no C_{60} layer) as the temperature was decreased, V_{LSSE} decreased with a slope change around 170 K, and this slope change has been attributed to the effective magnetic anisotropy change in YIG, due to spin reorientation transition.²⁵ However, all YIG/ C_{60} /Pt samples have shown an opposite temperature dependence of V_{LSSE} ; V_{LSSE} remains almost constant up to 200 K but below which it starts increasing exponentially (Fig. 5a). To better visualize this, the LSSE signal normalized to the signal at 140 K is shown in Fig. 5b. The exponential rise of V_{LSSE} below 200 K is evident from this figure, for all C_{60} -coated samples. All this suggests a dominant effect of C_{60} deposition on the LSSE signal in the YIG/ C_{60} /Pt systems.

It has been experimentally shown that the spin diffusion length of C_{60} possesses an exponential increase with lowering temperature just below 200 K when the film thickness is below 60 nm.³⁶ This logically relates the temperature dependence of V_{LSSE} to that of the spin diffusion length of C_{60} . In other words, the strong increase of V_{LSSE} with a temperature below 200 K can be attributed to the strong temperature dependence of the spin diffusion length of C_{60}

in this temperature region. To verify this, the $V_{\text{LSSE}}(T)$ data has been fitted to an exponential function that can be used to describe the temperature dependence of the spin diffusion length of C_{60} , and an example of this fit is shown in the inset of Fig. 5b. This result indicates that the long spin diffusion length of C_{60} has indeed played a crucial role in promoting spin transport in YIG/ C_{60} /Pt.

To quantitatively explain the C_{60} thickness-dependent LSSE behavior in the YIG/ C_{60} /Pt systems, we have adapted a model proposed by Lin *et al.* for YIG/NiO/Pt, in which the NiO layer is antiferromagnetic.¹² Although C_{60} is mostly diamagnetic in nature, we can still use this model. Due to the broad-spectrum distribution of nonequilibrium thermal magnons, we can assume that spins carried by magnons in YIG will be transferred to C_{60} similar to that of NiO, and due to the very weak spin-orbit coupling in C_{60} , they will easily be carried to the Pt layer. Since the exchange spin transport mechanism is dominant in the organic material C_{60} , the spin current can be written in the following form:

$$J_s^{\text{YIG}} = \frac{\frac{Pt}{C_{60}} \left(k \nabla T e^{-\left(\frac{x}{\lambda_{Pt}}\right)} \right)}{1 + G_{\text{YIG}} \left(\frac{1}{G_{Pt}} + \frac{1}{G_{C_{60}}} \right)} \frac{1}{\cosh\left(\frac{t_{C_{60}}}{\lambda_{C_{60}}}\right) + G_{C_{60}} \left(\frac{1}{G_{Pt}} + \frac{1}{G_{C_{60}}} \right) \left(\sinh\left(\frac{t_{C_{60}}}{\lambda_{C_{60}}}\right) \right)} \quad (2)$$

where k is the spin current coefficient, ∇T is the temperature gradient, G is the spin current conductance, λ is the spin diffusion length of the corresponding material, t_{C60} is the thickness of the C_{60} layer. Since it is difficult to obtain spin current magnitude from LSSE measurements, we have considered the ratio of the spin currents in both cases for our comparison purpose,

$$\frac{\frac{Pt}{C_{60}}}{J_s^{YIG}} = \left(1 + \frac{\left(\frac{G_{Pt}}{G_{C_{60}}} - 1 \right) G_{Pt}}{G_{Pt} + G_{C_{60}}} \right) \frac{1}{\cosh\left(\frac{t_{C_{60}}}{\lambda_{C_{60}}}\right) + G_{C_{60}} \left(\frac{1}{G_{Pt}} + \frac{1}{G_{C_{60}}} \right) \left(\sinh\left(\frac{t_{C_{60}}}{\lambda_{C_{60}}}\right) \right)} \quad (3)$$

In the spin-wave approximation,^{12,37} $\frac{G_{Pt}}{YIG}$ is proportional to $(T/T_C)^{3/2}$, where T_C is the Curie temperature of YIG. Since T_C of YIG is very high (~ 560 K), spin current injection should increase as a thin layer C_{60} is sandwiched in between YIG and Pt. This can explain the increased V_{LSSE} for YIG/ C_{60} (5nm)/Pt relative to YIG/Pt. It was previously reported that the insertion of a thin antiferromagnetic NiO layer (~ 1 nm) between YIG and Pt increased V_{LSSE} .¹² However, since λ of NiO is relatively small (~ 1 -2 nm), the hyperbolic function in the denominator of Eq. (3) increases, resulting in reduction of the spin current, as the NiO thickness is increased. In our case, as the thickness of the C_{60} layer is increased, both hyperbolic terms in Eq. (3) increase, resulting in an exponential decrease of V_{LSSE} . At the same time, reduction in H_{KS} in YIG/ C_{60} /Pt due to hybridization between the d_z^2 orbital of Fe and C atoms, which is evident from our TS studies and DFT calculations, would result in a net increase of spin moments at the YIG surface.²⁴ Also, it has recently been shown that the Stoner criteria for magnetism can be beaten in C_{60} by the metal-molecule interface and can induce a magnetic moment in the metal surface.²³ Theoretical studies have shown that increase in surface magnetic moment density increases the spin mixing conductance.¹⁴ This explains our observation of the enhanced V_{LSSE} at room temperature in YIG/5nm C_{60} /Pt for both single crystal and thin film³⁸ of YIG as compared to YIG/Pt, when $\lambda_{C_{60}}$ is relatively small at room temperature (~ 12 nm). The decrease in V_{LSSE} with increasing the C_{60} thickness ($t_{C_{60}}$) for the YIG/ C_{60} /Pt systems can be described by the relation $V_{LSSE} \propto e^{-t/\lambda}$.³⁹ Fitting the C_{60} thickness-dependent V_{LSSE} data of YIG/5nm C_{60} /Pt at 300 K to this equation has yielded $\lambda_{C_{60}} \sim 11 \pm 2$ nm, which is similar to that reported for the $Ni_{80}Fe_{20}/C_{60}/Pt$ system ($\lambda_{C_{60}} \sim 13 \pm 2$ nm at 300 K) using the spin pumping method.³⁹ This indicates that the C_{60} spin current arriving at the C_{60} /Pt interface is proportional to $e^{-t/\lambda}$.

4. Conclusions

In conclusion, we have demonstrated a new, effective approach for enhancing the LSSE in a ferromagnetic insulator/metal system like YIG/Pt by adding a thin, intermediate layer of high spin diffusion length organic semiconductor like C_{60} . We have shown that the presence of C_{60} reduces significantly the conductivity mismatch between YIG and Pt and the surface magnetic anisotropy of YIG, giving rise to the enhanced spin mixing conductance and hence the enhanced LSSE. Results from our first principles simulations demonstrate that the density of carriers at the Fermi level is much enhanced upon inclusion of the interface C_{60} layer, which is also accompanied by a reduced magnetic anisotropy. The LSSE of YIG/ C_{60} /Pt strongly depends on the spin diffusion length of the intermediate layer C_{60} ; the temperature dependence of LSSE resembles that of the spin diffusion length of C_{60} . Our study provides a pathway for designing novel hybrid materials with prospective applications in spin caloritronics and other multifunctional devices.

Conflicts of interest

There are no conflicts of interest to declare.

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Author contributions

V.K., R.G. and R.D. had equal contributions to the work. M.H.P. and T.N. developed the initial concept. V.K., R.D., R.G., T.N., and M.H.P. designed the study. YIG/ C_{60} samples were fabricated by R.G. and M.P. YIG/ C_{60} /Pt samples were fabricated by V.K. and R.D. Structural and magnetic characterization, and spin Seebeck effect measurements were performed and analyzed by V.K., and R.D. A.P. and L.M.W. performed DFT calculations and simulations. All authors discussed the results and wrote the manuscript. M.H.P. and H.S. jointly led the research project.

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