Ionic Modulation of the Interfacial Magnetism in a Bilayer System Comprising a Heavy Metal and a Magnetic Insulator for Voltage-Tunable Spintronic Devices

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The voltage modulation of yttrium iron garnet (YIG) is of practical and theoretical significance; due to its advantages of compactness, high-speed response, and energy efficiency, it can be used for various spintronic applications, including spin-Hall, spin-pumping, and spin-Seebeck effects. In this study, a significant ferromagnetic resonance change is achieved within the YIG/Pt bilayer heterostructures using ionic modulation, which is accomplished by modifying the interfacial magnetism in the deposited “capping” platinum layer. With a small voltage bias of 4.5 V, a large ferromagnetic field shift of 690 Oe is achieved in heterostructures of YIG (13 nm)/Pt (3 nm)/(ionic liquid, IL)/(Au capacitor). The remarkable magnetoelectric (ME) tunability comes from the additional and voltage-induced ferromagnetic ordering, caused by uncompensated d-orbital electrons in the Pt metal layer. Confirmed by first-principle calculations, this finding paves the way for novel voltage-tunable YIG-based spintronics.

YIG—a commonly used magnetic material—has a high Curie temperature ($T_C \approx 650$ K), a very low intrinsic damping constant ($\alpha \approx 10^{-7}$), a long spin-transmitting length ($=1$ cm), a broad bandgap ($E_g \approx 2.85$ eV), and a very narrow ferromagnetic resonance (FMR) linewidth ($=1$ Oe). It is an ideal ferromagnetic insulator, exhibiting plenty of spintronic properties, including spin-pumping,[4] spin-Hall,[5] spin-Seebeck,[4,6] and magnetic proximity effects (MPE).[7,8] Recently, research efforts involving spin–orbital torque (SOT) have focused on the coupling of heavy metals and magnetic metals or insulators; in particular, current-driven SOT has been reported for YIG/(heavy metal) heterostructures.[9–15] In 2013, Sun et al. discovered that a Pt thin film (>3 nm) on a YIG layer results in damping accompanied by a strong FMR shift due to MPE, where dynamic exchange coupling leads to the ferromagnetic (FM) ordering of Pt near the YIG/Pt interface.[15] Most recent progress has focused on how to induce additional interfacial magnetism in Pt using electric fields at very low temperature.[16,17] Meanwhile research efforts have not yet discussed how the interfacial ME effect influences the thin-film properties of YIG or how it affects the magnetism of the entire bilayer system.

If the interfacial properties between Pt and YIG can be modified by a localized electric field (E-field) via a voltage-induced Fermi-level shift, any earlier disadvantages of YIG-related spin effects could be overcome, resulting in faster, more compact, and more energy-efficient voltage modulation. This approach also provides a new option for researchers targeting voltage-controllable spin-Hall, spin-pumping, and SOT effects. Here, we utilize an ionic liquid gating (ILG) approach for ferromagnetic modulation; an IL serves as an effective gating medium that provides significant interfacial charge accumulation under an E-field.[16,18–21] ILG...
can manipulate the interfacial magnetism of metallic ultrathin films by changing the electron density at the Fermi level,[18] can modulate the magnetism of oxide thin films by changing oxygen vacancies,[19,20] and can even trigger the tri-phase transformation in some oxides by controlled ionic doping.[21] Compared with conventional multiferroics, using ILs has significant advantages, such as room-temperature operation, a low gate voltage (Vg < 5 V), high magnetoelectric (ME) tunability, and compatibility with various substrates.[22]

In this work, a series of YIG thin films with different thicknesses (7–35 nm) were epitaxially deposited onto single-crystal substrates of gadolinium gallium garnet (Gd3Ga5O12, GGG). Heavy-metal Pt thin films were then added, to serve as the coupling media between the YIG layer and ionic liquid (IL) and as one of the electrodes of the gating process. By applying an IL layer onto these YIG/Pt heterostructures, we established an ideal capacitor structure; a small Vg (<5 V) was then applied across the IL layer. Subsequently, for the 13-nm YIG film at −110 °C, a large FMR shift of 690 Oe was obtained. In contrast, previous Pt gating efforts[16,17] produced a relatively weak tunability of the E-field-induced magnetism, and they were carried out at a much lower temperature. The first-principle calculations demonstrated that the enhancement of spin ordering and the corresponding FMR shift result from the additional and electrically induced FM ordering in the Pt metal layer during the ILG process. Earlier simulation results revealed that the additional FM ordering is caused by both the uncompensated d orbital electrons of Pt6+ and a Fermi-level shift due to the E-bias.[23] We believe that this recently discovered ME gating mechanism—where FM ordering is ionically enhanced in the heavy metal layer—will attract further attention because YIG/Pt and other YIG/(heavy metal) heterostructures are well-known SOT systems, which continue to be a research hotspot. Additionally, YIG is a perfect medium for radio-frequency (RF) and microwave devices—such as filters,[23–25] shifters,[26] isolators,[27] circulators, spin-wave components,[9,10,28] and ultra-low-power dissipation devices,[29] as well as for optical devices.[30] The E-field manipulation of YIG is thereby of great significance in obtaining voltage-tunable YIG devices with more compactness, higher-speed response, and higher energy efficiency.[25,31,32] The large FMR tunability in YIG-based heterostructures also has application potential in tunable RF/microwave devices, such as band-pass filters, as well as in tunable spintronics devices, such as spin-wave transistors.

Pulsed laser deposition (PLD) was used to deposit YIG onto GGG (111) substrates at thicknesses of 7, 13, and 35 nm. Figure 1a shows the X-ray diffraction (XRD) pattern of a sample with a 35-nm YIG layer; it indicates that the YIG film was oriented in the (111) direction. The inset of Figure 1a shows an ultra-flat surface morphology of the as-grown sample observed using atomic force microscopy (AFM). Figure 1b shows cross-sectional transmission electron microscopy (TEM) images of the GGG/YIG (35 nm)/Pt (3 nm) sample, revealing good epitaxy of the YIG layer from the GGG substrate. The in-plane magnetic hysteresis loops of the YIG (35 nm) sample before and after capping with the 3-nm Pt film are compared in Figure 1c. The hysteresis loop after Pt deposition becomes more quadrate in shape, indicating enhanced FM ordering. Electron spin resonance (ESR) is a very powerful method for quantitatively measuring the spatial magnetic anisotropy of these samples, and for obtaining FMR measurements. Figure 1d shows the ESR spectra of 35-nm YIG, as a bare substrate and capped with 3-nm Pt. With Pt capping, the in-plane resonant field (Hr decreased and the out-of-plane Hr increased, implying a strengthened FM ordering and an equivalently increased in-plane magnetic anisotropy, which is consistent with the shape change of the hysteresis loop after Pt capping. We attribute this interfacial phenomenon to MPE, which comes from the interfacial coupling of the YIG and Pt layers.

The ILG process was monitored within the ESR cavity; the geometry of the in-situ ESR measurements is shown in Figure 2a. The sample could be rotated using the sample holder to modify the magnetic field direction with respect to the normal of the substrate’s surface (Figure 2b, inset). The precession of the magnetic moment of the sample is resonant with the applied microwave when the magnetic field H is equivalent to the resonant magnetic field Hr; this FMR effect can be expressed with the Kittel formulas:

\[
f = \left( \frac{g \mu_B}{2 \pi} \right) \sqrt{H_r^2 + H \cdot M_s} \quad (1)
\]

for the in-plane condition and

\[
f = \left( \frac{g \mu_B}{2 \pi} \right) (H_r - M_s) \quad (2)
\]

for the out-of-plane condition.[33] f is the frequency of the microwave in the cavity; \( \gamma = 2 \pi = 2.8 \text{ GHz kOe}^{-1} \) is the literature value of the gyromagnetic ratio;[34] and Ms is the saturation magnetization. All FMR measurements were carried out at a microwave frequency of 9.2 GHz. Under a positive Vg, the bis(trifluoromethylsulfonyl)imide anions (TSFI−) and the N,N-diethyl-N-(2-methoxyethyl)-N-methylammonium cations (DEME+) of the IL migrated toward the Au and Pt electrodes, respectively. The anions generated an enormous surface charge density of up to \( 10^{15} \text{ cm}^{-2} \), producing a strong E-field at the Pt/IL interface. Figure 2b shows the dependence of the FMR field on the angle \( \theta \) between the magnetic field and the normal of the sample surface. The angular dependence is shown for the as-grown YIG/Pt heterostructure and for a sample under a 4.5-V IL gate voltage; additionally, the angular dependence of the ILG-induced FMR shift is studied. At room temperature, a maximum FMR shift of 26 Oe was achieved in the out-of-plane direction for the YIG (35 nm)/Pt sample. Figure 2c demonstrates how the ESR spectrum sequentially shifts after an increase in gating bias voltage across the IL layer on the GGG/YIG (13 nm)/Pt (3 nm) sample with the external magnetic field parallel to the normal direction of the surface. In Figure 2c, the out-of-plane FMR response shifted 123 Oe toward the high end (larger FMR). After the removal of Vg, the FMR curve moved towards the initial state. We noticed that only a positive E-field improved the MPE and FM ordering. In contrast, a negative Vg did not affect the magnetic properties (see Supporting Information, SI: Figure S4).

The influence of YIG thickness and ambient temperature during the ILG process was also analyzed. The thickness dependence of the Hr shifts arising from ILG (Vg = 4.5 V) and
from Pt deposition are shown in Figure 3a. The similarity in the thickness dependence of the FMR shifts due to Pt capping and due to ILG indicates that ILG essentially results in an interfacial effect. Interestingly, as shown in Figure 3b, a much greater FMR shift of 690 Oe with the out-of-plane magnetic bias was achieved at $-110^\circ$C via ILG in the YIG (13 nm)/Pt (3 nm) sample. Although the FMR shift in the sample with 13-nm YIG is much larger than that of the sample with 35-nm YIG, the FMR signal is weak for the 13-nm-YIG sample. As a result, for better accuracy, we chose a sample with 35-nm YIG to study the temperature dependence of the tunability of ILG. The shift between $V_g = 0$ and 4.5 V is shown in Figure 3c for both in-plane and out-of-plane directions for a YIG (35 nm)/Pt sample. With decreasing temperature, there appeared to be stronger MPE evidenced by a larger $H$ difference between the in-plane and the out-of-plane directions. This effect comes from enhanced ordering in the YIG/Pt system, and has appeared in other multiferroic systems, such as spin waves in LSMO/PMN-PT (a thin film containing La, Sr, and Mn on a substrate with Pb, Mg, Nb, and Ti)[35] and perpendicular magnetic anisotropy (PMA) structures.[36]

The reversibility of the FMR switching was also studied in the GGG/YIG (35 nm)/Pt (3 nm) sample along both the out-of-plane and in-plane directions (Figure 3d; also see SI: Figure S5). The $H$ could be switched back and forth (from 2198 to 2204 Oe in-plane; from 5735 to 5760 Oe out-of-plane) with an alternative $E$-bias polarity across the IL layer at room temperature, indicating great reversibility.

Many reports have demonstrated the existence of MPE.[7,8,11] In a normal metal, several atomic layers capable of FM ordering become very similar to a FM material; this description can be applied to the interface of the YIG/Pt heterostructures. Sun et al. had clarified that the shift in the FMR curve is caused by MPE,[15] and Liang et al. studied the dependence of MPE strength on the interface structure by using first-principles calculations based on density functional theory (DFT).[37] They claimed that the FMR shift originated from the direct exchange interaction between the Fe 3d and Pt 5d electrons via electronic state hybridization and the electron exchange coupling among the Pt atoms. In our experiments, the positive $V_g$ resulted in an enrichment of cations at the Pt/IL interface, which then caused electrons in the Pt to migrate to the interface, thereby

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**Figure 1.** Material properties and MPE in the YIG/Pt system. a) XRD of the GGG/YIG (35 nm)/Pt (3 nm) sample. The inset shows the surface morphology of the as-grown film according to AFM. b) Cross-sectional TEM images of the GGG/YIG (35 nm)/Pt (3 nm) sample. c) Room-temperature in-plane normalized magnetic hysteresis loops of the YIG (35 nm)/Pt (3 nm) (red triangles) and the bare YIG (35 nm) (green squares) samples. $H$, $M$, and $M_s$ refer to the magnetic field, magnetization, and saturation magnetization, respectively. Inset shows the geometric relationship between the sample and the magnetic field direction. d) ESR spectra of the bare YIG (green) and YIG/Pt (red) samples for both in-plane and out-of-plane directions at room temperature. $P$ and $H$ are the power absorbed by the sample and the static magnetic field, respectively.
enhancing an MPE-like effect in the YIG/Pt heterostructures. In contrast, the ionic gating effect of a YIG/Cu heterostructure has negligible ME tunability (see SI: Figure S6). To further understand the mechanism behind the gating process, we pursued the relevant theoretical calculations.

We pursued first-principle calculations using the VASP (Vienna ab-initio simulation package) code\cite{38,39} to understand what was happening after application of the ILG; Figure 4a depicts the atomic modeling of the YIG/Pt heterostructure. The calculations were based on DFT and the generalized-gradient approximation (GGA) with an interpolation formula according to Vosko, Wilk, and Nusair\cite{40} and a plane-wave basis set within the framework of the projector augmented wave (PAW) method.\cite{41,42} The cut-off energy for the basis was 500 eV, and the convergence criterion for the electron-density self-consistency cycles was $10^{-6}$ eV. In the Brillouin zone, we sampled $(15 \times 15 \times 15)$ k-point grids using the Monkhorst–Pack scheme\cite{43} to make sure the results converged. As shown in Figure 4a, application of ILG generates an E-field along the Pt-to-YIG direction; however, it is difficult to build up a chemical potential shift in metals due to the strong screening effect. The electrons of the Pt layer are forced to the Pt/IL interface, leaving positive states at the YIG/Pt interface. The charge accumulation also builds a reverse E-field to balance that from the IL. In this case, numerically, when a $V_g$ is applied, the IL will shift the nearest Pt atom by an energy of $eV_g$, where $e$ is the elementary charge; the platinum at the Pt/IL interface then takes on negative charge states (Pt$^{n-}$, $n = V_g$). In contrast, the platinum at the YIG/Pt interface becomes positively charged, Pt$^{n+}$, in order to neutralize the total system.

We then questioned whether this enhanced MPE-like effect has any contribution from the non-zero Pt state that arose from the ILG. Using a face-centered cubic (fcc) Pt model (Figure 4a), the magnetization of Pt was calculated as electrons were added or removed. Because platinum is a heavy metal, the spin–orbit coupling effect was also considered. We chose Pt$^{5+}$ for the Pt at $V_g = 5$ V and chose Pt$^0$ at $V_g = 0$ V, in order to conduct a detailed analysis of the gating effect. The density of states (DOS) in Pt$^0$ showed a strong energy dependence, and integration of each orbital type revealed that the valence
electrons of Pt$^0$ (10 electrons per Pt atom, 5d$^9$6s$^1$) are mainly d electrons. However, the specific numbers are not correct because we only summed the charge density inside the atomic sphere of Pt while neglecting the charge density found in the gaps between the atomic spheres. In the Pt$^{5+}$ state, when the Fermi energy was pushed to a much lower energy position, the s and p orbitals almost vanish, leaving only d orbitals, which means that the valence electron of Pt$^{5+}$ can be denoted as 5d$^5$.

**Figure 3.** Thickness dependence and temperature dependence of the ILG tunability and the switching behavior of the ILG process. a) YIG thickness dependence of the FMR shift as a result of the Pt deposition (red triangles) and as a result of the ILG on the YIG/Pt system (blue squares), along the out-of-plane direction at $-110^\circ$C. b) The out-of-plane ILG-induced FMR shift at $-110^\circ$C of YIG (13 nm)/Pt/IL/Au at a $V_g$ of 4.5 V, along the out-of-plane (blue squares) and in-plane (red circles) directions. c) Temperature dependence of the FMR shift of YIG (35 nm)/Pt/IL/Au at a $V_g$ of 4.5 V, along the out-of-plane (blue squares) and in-plane (red circles) directions. d) Reproducibility tests of the gating process in YIG (35 nm)/Pt (3 nm) along the out-of-plane direction at room temperature.

**Figure 4.** First-principle calculations of the ILG in the YIG/Pt system. a) Schematic of the YIG/Pt/IL/Au system, showing the atomic structure used for simulation. In the portion showing the IL, [DEME]$^+$[TFSI]$^-$, black, dark grey, light blue, red, brown, and light green spheres represent C, H, N, O, S, and F, respectively; EDL indicates the electrical double layer. b,c) The density of states (DOS) as a function of energy for Pt$^0$ (b) and Pt$^{5+}$ (c). The DOS data were separated into s- (blue data points), p- (red), and d- (orange) orbitals, and all three data sets were integrated (int) over energy (relative to the Fermi energy, $E_E^-$) to analyze the occupation of the corresponding orbitals (as indicated by the curves of the corresponding color). e,f) The spin density plots of the d-orbital for Pt$^0$ (e) and Pt$^{5+}$ (f). Here $m_x$, $m_y$, and $m_z$ represent the projection of spin density along the $x$, $y$, and $z$ axes, respectively.
The spin density was also simulated, for each orbital type of Pt\(^0\) and Pt\(^{5+}\). The results are plotted in Figure 4d,e (also see SI: Figure S7). It is obvious that the s and p orbitals of both Pt\(^0\) and Pt\(^{5+}\) barely make any contribution to the magnetization. However, analysis of the d orbitals of Pt\(^0\) and Pt\(^{5+}\) reveal different features. Pt\(^0\) has a slight spin density that vibrates around zero, but it ends up as non-magnetic after the total Fermi sea is considered. The spin density of Pt\(^{5+}\) has a much stronger energy dependence; it can be three magnitudes larger than that of Pt\(^0\) at the same energy level, and after evaluating the entire Fermi sea, Pt\(^{5+}\) has a non-trivial magnetization.

Using Hund rules, magnetization on every Pt\(^{5+}\) atom can be easily deduced, so strong exchange interactions between Pt\(^{5+}\) and magnetic materials were expected, and the experimental results are consistent.

According to the calculations, we found that platinum ions with approximately 5 positive charges (Pt\(^{5+}\)) suddenly exhibit a strong magnetic moment, which was even slightly larger than that of Ni. When the \(V_g\) was around 5 V, we found a MPE enhancement at the YIG/Pt interface and an additional FM ordering in the Pt layer. The estimated gate voltage (5 V) is consistent with the experimental data (4.5 V), which indicates that a sudden magnetic enhancement may arise with applied voltage (Figure 5a,b). The theoretical enhancement of the FM ordering was estimated as \(\approx 720\) Oe, which is very close to the experimental result of 690 Oe. In general, the simulation results agree very well with the experimental results. The tunability of the FMR using ILG in the YIG/Pt bilayer paves the way for low-voltage-tunable microwave-response devices. A conventional YIG-based microwave-response device is driven

![Figure 5. YIG/Pt- and YIG/Pt/IL-based microwave-response devices. a) The measured \(H_r\) field as a function of increasing \(V_g\). The inset shows the geometry of the sample in the \(H\) field. b) The calculated magnetization of Pt as a function of the electron charge of Pt; e.g., a charge of 5 represents face-centered cubic Pt\(^{5+}\), where each platinum has lost 5 electrons. \(\mu_B\) represents the Bohr magneton. Inset: Schematic of the electron distribution after the gating process; here we only show the charge accumulation near the interfaces. c) Conventional tunable microwave device, driven by DC current. \(H_{\text{min}}\) and \(H_{\text{max}}\) represent the minimum and maximum magnetic field, respectively, that define the device’s response range. d) Novel YIG/Pt/IL-based microwave device that is voltage-tuned using a settled external magnetic field, \(H_{\text{set}}\). The frequency response range comes from the ILG process.](advmat.de)
by a DC (Figure 5c). With increasing current, the resonance frequency will have a greater shift, which can be deduced by the Kittel equation (see Equation (1) and (2)). Using the ILG technique (Figure 5d) at a chosen external field, MPE at the YIG/Pt interface induces the FMR to shift, revealing tunable magnetic properties using low \( V_g \) values. Compared with the conventional microwave devices, the ILG-based device is more energy-efficient and far more compact due to the zero DC drive magnet. In addition to microwave devices, spintronic devices may be possible by extending this idea and replacing the Pt in the YIG/Pt/IL system with other heavy metals.

In summary, by considering the ionic modulation of the magnetic ordering in the YIG/Pt bilayer and how the resulting interfacial charge accumulation may enhance the FM ordering and shift the FMR, we have realized voltage regulation of YIG thin films using a capacitor IL gating structure. The outstanding ME tunability is quantified by the 690-Oe FMR shift of the YIG-based heterostructure; this is an order of magnitude greater than the tunability of previously reported YIG-based systems, and it corresponds to a much greater ME Figure of merit of 14, which is defined as the ratio between ME tunability and the FMR shift. The first-principle calculations revealed a novel E-field-induced FM ordering in capping Pt layer and a corresponding tunability in the FMR via the gating process. ILG in YIG/heavy metal systems is of great research interest and practical significance because it has potential application in high-performance voltage-tunable YIG-based devices.

**Experimental Section**

**Sample Preparation:** Fifteen YIG/Pt heterostructure samples were produced, with sets of five having a YIG thickness of 7, 13, or 35 nm. In all samples, the Pt thin film was 3-nm thick. The YIG films for IL gating were deposited on \( \text{Gd}_2\text{Ga}_2\text{O}_12 \) (111) by PLD. During deposition, the temperature of the substrate was maintained at 800 °C while the oxygen pressure was 13 Pa, and the laser pulse rate was 1 Hz. After depositing, the films were annealed in situ under 5.4 × 10⁴ Pa of oxygen pressure with a cooling rate of 2 °C s⁻¹. After cooling down to room temperature, the YIG films were transferred to the magnetron sputtering chamber. A Pt layer was subsequently deposited onto these YIG films.

**Magnetic Properties:** Magnetic hysteresis loops of the samples were measured using a LakeShore 7404 vibrating sample magnetometer (VSM). Because the magnetization of the YIG films is small (~20 emu), only the in-plane magnetic hysteresis loops of these samples were displayed. FMR curves of the samples were measured using an X-band ESR system (JOEL, JES-FA200). The change in magnetic anisotropy and the spin-wave patterns were precisely determined.

**ILG Preparation:** We chose the IL, [DEME][TFSI]⁻, as the gating material because of its potential tunability and well-studied physicochemical properties. A grid structure, Pt/IL/Au, was formed using Au and Pt as the gating electrodes. \( V_g \) values from 0 to 4.5 V were applied to the grid structure using a Keysight B2901A Precision Source/Measure Unit. In the IL phase, the anions and cations migrated toward the Au and Pt electrodes, respectively, driven by the E-field. The charge carrier ions generated an enormous surface charge density of up to 10¹¹ cm⁻², producing a strong interfacial E-field. The influence of the E-field on the magnetic properties of these samples was studied using in-situ ESR and VSM measurements. During the gating process, low-temperature FMR curves were measured in a cryogenic chamber with liquid \( N_2 \). The E-field-induced FMR shifts in all samples had good reversibility.

**Structure and Morphology Analysis:** The structure of samples were analyzed using high-resolution powder XRD (Bruker D8 ADVANCE). The microstructure and morphology of cross-sections of the samples before and after the gating process were imaged using high-resolution TEM (JEOL JEM-ARM 200F).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

interfaces, ionic liquid gating, magnetism, magnetoelectric coupling, yttrium iron garnets

**References**
