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Spinterface: A new platform for spintronics

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ABSTRACT

Since its discovery in early 2000's Molecular Spintronics has developed in an established and fructuous research field, achieving a number of outstanding results and unveiling unusual spintronic properties. Typically the most mysterious device element, the interface, in molecular spintronics has on contrary received and enormous attention and even gained a special nickname – the spinterface. Based on significant efforts of many research groups worldwide it has been established its critical role in defining the main functionalities of molecular spintronic devices. Noteworthily the spinterface was found to control the properties of the both components constituting the interface, not only those of the molecular layer but surprisingly also those of the magnetic counterpart. This paper aims to overview the most striking spinterface properties and to highlight the possibilities to promote new device paradigms based on interfacial modulation.

1. Introduction

In interfaces and surfaces, the breaking of translational and inversion symmetry is responsible for a number of electronic effects with consequences for functional properties. Such concept enters into great consideration of the description of magnetic correlations [1]: surfaces can have different magnetic moments than the corresponding bulk, interfaces can produce new magnetic states including creating magnetic moments from non magnetic materials as local coordination chemistry and band structure are modified or even determining proximity induced ferromagnetism with intensity decreasing from the interface. Such concepts have been deployed in a number of spintronic devices and the ability to reliably describe and control the magnetic properties of interfaces is essential to understand and design their functionality. The introduction of molecular materials in spintronics make this aspect more and more decisive [2]: molecules conveniently tailored with chemically designed function can be interfaced with ferromagnetic (FM) contacts and/or be embedded into devices to properly tune the overall functionality [3]. Starting from the first experimental evidence of positive and negative magnetoresistance behaviour in the same spin valve structure depending on the thickness of the organic spacer [4], it was clear that the spin behavior in molecular devices was strictly dependent on the nature of the chemical bonds between the organic molecules and the magnetic electrodes. Soon after the concept of "spinterface" appeared [5]: spin dependent interfacial states can control the spin functionality of molecular devices being able even to invert the spin polarization of the current extracted from a ferromagnetic electrode. This effect has become then hot topic in molecular spintronics showing a plethora of complex interfacial magnetic behavior.

In this paper we intend to present major achievements in the field of spinterface. After a brief introduction about the phenomena occurring at the metal/organic interfaces, we focus on the magnetic aspects discriminating between effects on the ferromagnetic and molecular side respectively. Finally, we propose some future perspectives for spin manipulation by interface engineering.

2. Molecule-metal interfaces

Contact between a metallic surface and a conjugated organic molecule results in a variety of effects occurring at the interface in reason of the electron density re-distributions of both metal and molecule. This rearrangement can be accompanied by changes of bond lengths and thus a structural relaxation or deformation of the molecule and/or the metal surface atoms may take place. Such interaction is often classified between the two extreme cases of physisorption (weak interaction) and chemisorption (strong interaction) as shown in Fig. 1. Physisorption is characterized by the absence of chemical bonds and the molecule generally retains its gas phase electronic structure, although some distortion is still possible. The binding energy depends on the polarizability and varies between few meV up to fraction of eV, the adsorbate–substrate

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Fig. 1. Schematic illustration of the energy level alignment between a molecule and a 3d metallic surface(left). Depending on the strength of the molecule-surface interaction, physisorption(middle) or chemisorptions(right) take place.

equilibrium distance is typically $\geq\!\!3 \text{\AA}$ and the interaction is mainly mediated by van-der-Waals forces. Chemisorption is instead characterized by strong perturbation of the molecular electronic structure with formation of chemical bonds with the substrate that in turns can be subjected to a deformation too. Depending on the electronic distribution, covalent or ionic bonds are formed between the atoms or molecules and the surface. Typically two phenomena can occur: charge transfer and/or hybridization [6]. In charge transfer phenomena, the orbitals of molecular entity cross the Fermi energy of the metals causing a redistribution of the charge occupancy. Conversely, the hybridization phenomena are characterized by a broadening of the molecular orbitals and the subsequent formation of additional electronic states with mixed molecular and metallic character. Such strong modifications on the interfacial configuration due to chemisorption impact on the density of states, the interfacial energetics (barrier, dipoles) and the consequently the charge injection property of the device. The understanding of the mechanism at interfaces is the key to enable the tuning of device performances. This effect could be even more critical if we look after the spin resolved electron distribution, leading to the so called Spinterface. While physisorption does not sense any spin splitting of molecular states (even if long-time spin-dependent electron dynamics has been observed in a physisorbed organic layer on a specific configuration [7]), chemisorptions can be characterized by spin dependent broadening of initially discrete molecular levels, by spin dependent injection barrier and by hybridized states with strong spin selection rules, all being key factors that influence the spin and charge injection across the interface. In this framework, the organic/ferromagnet interface can be envisaged as a distinct and complex system with characteristic properties depending on the specific of bonding at the interface. Modification of the magnetic state can in fact be detected in both the inorganic and organic side of the interface. From the inorganic point of view, the variation of local electronic structure is responsible for emergent magnetism from usually non (dia)magnetic metals or leading to magnetic hardening or even magnetic suppression in ferromagnetic materials. On the molecular side, they may even present spin unbalance, featuring magnetic coupling with a ferromagnetic substrate or acting as spin filtering elements in case of hybridization phenomena. Moreover additional functions of molecular units such as switchability by external parameters (light, voltage) can be used to manipulate the response of the molecular unit providing a unique method for a multifunctional operation. In the following we discuss in details the effects of interaction molecule-substrate on the ferromagnet and on the organic layer separately highlighting the spinterface effects.

2.1. Spinterface effects on ferromagnetic metal side

It has long been investigated in 3d-ferromagnetic thin films that the discontinuity in the atomic structure at the outmost surface layer is an important factor affecting the overall macroscopic film properties: surface magnetization profile can be significantly different from the bulk one with even an enhancement in the magnetic moment of the outermost

surface layer [8]. In the same way, when a molecule is chemisorbed onto a ferromagnetic surface, the strength of the interaction and the consequent orbital distortion or hybridization has an impact on the overall property of the magnetic inorganic layer. This topics started to be investigated in the 90's to elucidate the catalytic behavior of magnetic clusters: seminal works [8–11] focus on the adsorption of simple mono and diatomic molecular species like O, NO or CO that could reduce, or even quench, the magnetic moment of a surface layer [12].

When polyatomic molecules with more complex geometrical configuration are taken into account, the scenario become even more complex and a predictive activity via DTF calculation is often needed to guide and support the experimental findings.

To estimate how the absorption of a molecule affect the magnetic behavior of a ultra thin film through the modification of the surface states we need to briefly remind the main energetic terms determining the magnetic configuration [13]. Exchange interaction is at the origin of magnetic order (either parallel or anti parallel alignment) of the spins at the lattice site caused by the overlap of electronic wave functions; it is measured by the exchange integral J [14]. This term includes a variety of phenomena, such as direct exchange, long-range oscillating Ruderman-Kittel (RKKY) exchange mediated by conduction electrons, indirect exchange mediated by other elements and double exchange involving charge fluctuations. The second energetic term refers to the magnetocrystalline anisotropy (MCA), a quantum relativistic effect caused by spin orbit interactions. Electrons orbits are linked to the crystallographic structure and, by their interactions with spins, a preferential orientation along specific crystallographic axis is favored. Another anisotropy contribution which is particularly important in ultrathin films is the surface magnetic anisotropy (SMA), first identified by Neel, and which arises from the break of symmetry at the interface and depends on the surface morphology. Other forms of anisotropy include the shape anisotropy (DMA) that originates from the classical interaction between dipoles. Anisotropy terms (MCA; SMA, DMA) are usually small $(\sim 10 \mu eV/atom)$ compared to the exchange energy (0.1 eV/atom). This implies that the magnitude of the magnetization M is determined almost by the exchange energy while anisotropy terms define the spatial direction of the magnetization vector [15]. Typically, magnetization direction is solved by finding the minimum energy configuration. It is clear that upon adsorption of a molecular specie, frontier wave functions are perturbed and consequently the magnetic terms are re-balanced. This is the case of absorption of zinc methyl phenalenyl (ZMP, C14H10O2Zn) onto Cobalt layer [16]: for the hybridized Co surface, the exchange coupling J value was reduced by nearly 70% compared to a clean Co surface and became comparable the surface anisotropy. As a result, the magnetic configuration of the thin film is re-defined leading to a magnetoresistance of the interface is decoupled from that of the bulk and the typical quantity associated to the hysteresis cycles (switching fields and saturation) modified.

The adsorption of an organic molecule is an effective strategy to manipulate the local magnetism of a magnetic substrate (see Fig. 2).



Fig. 2. (a)Saturation magnetization suppression and coercivity enhancement of Co thin film for varying film thicknesses of C_{60} overlayer at 100 K. From Ref. [27] (b) Spin-resolved photoemission spectra as a function of the binding energy for 15 ML Co/Cu(001) (top panel); 1.1 ML phenanthroline/Co (middle panel) after subtraction of metallic Co spectrum ("Co") and for 1.4 ML pentacontane/Co (bottom panel). The photon energy is 20 eV. The corresponding molecules are depicted as inset [30].

Remarkably, the magnetic anisotropy of a magnetic thin film- an important parameter for magnetic data storage devices [17]- can be modified by the absorption of a non magnetic molecule. Spin re-orientation transition from in-plane to out-of-plane magnetization upon covering ultra thin Co layer with a self-assembled monolayer of alkanethiolates [18], small molecules(quinolines) [19] or buckminsterfullerene (C₆₀) [20] has been demonstrated due to the enhancement of the magnetic anisotropy energy terms as result of the hybridization between organic π and Co d frontier orbitals. Magnetization switching of ferromagnetic thin layers can be induced solely by adsorption of chiral molecules [21] by combining chiral-induced spin selectivity and charge transfer effects. On the contrary a reduction of the anisotropy term has been predicted for C₆H₆ on Fe [22]. Changes in the anisotropy energy can be detected by variation of the magnetic hysteresis cycles: the electron acceptor tetracyanoquinodimethane (TCNQ) slightly reduces the coercivity of a Co layer, while the electron donor tetrathiafulvalene (TTF) increases the coercivity by a factor of \sim 1.5. These complementary effects indicate that magnetic hardening or softening can be tuned also by interfacial orbital occupancy [23,24]. Several papers computed the effect of chemisorptions on magnetic quantities of epitaxial metallic ferromagnetic metals [16,25-28]. Typically the first-principle based approaches evaluate the effects of surface geometry and structural rearrangement on the exchange integral J and on the anisotropy terms. Starting from microscopic quantity, the magnetization reversal process is simulated by Montecarlo methods by identifying the model Hamiltonian for the ferromagnetic layer [29], and then hysteresis loop and temperature dependence of the coercive field are deduced. Same approach has been carried out to compute the spin polarization of surface layer [30] as shown in Fig. 2b. As expected hybridization can lead to surprising effects: inversion of spin polarization of a Fe layer is obtained upon the deposition of Co-Phthalocyanine(Pc) [31] or of a Ferromagnetic Heusler alloy Co₂MnSi(001) upon the absorption of C₆H₆ [32], or complex spin configuration including sublattice antiparallel alignment of Fe₄N upon the absorption of benzene [33]. Interfacial hybridization effects can be employed to manipulate spin injection efficiency as in case of buckminsterfullerene on magnetite Iron oxide(C₆₀)/Fe₃O₄, where, by electronic charge rebalancing, an enhancement of the charge conductivity and a preservation of half-metallic property of FM oxide has been detected [34]. For the above examples, it is clear that DFT studies still

play also an important role in predicting and interpreting the experimental findings about changes in the magnetic behaviour of ferromagnetic thin film [3]. Pushing forward this modulation of magnetic properties by increasing the number of interfaces with molecules, graphene–Co multilayer possess a strong and robust effective magnetic anisotropy that linearly increases as a function of heterostructure thickness; such behaviour can be opportunely tuned to promote large anisotropy in small size spintronic devices [35]. It is worth noting that the effect of interfacial interaction can extend all over the entire magnetic layer making molecules as tuning elements with important effect on standard spintronics. Remarkably, it is not only the interface which affects the overall magnetic behavior: the magnetic hardening of the Co film depends on the thickness of the molecular layer and it is effective up to 200 nm of C_{60} organic film [27].

Molecules can act on the dynamics of ferromagnetic layer by changing the magnon damping as in the case of Co covered by 1-(2-bisthienyl) benzene [36] and increasing the spin diffusion length. Even more complex magnetic interaction can be found between isolated Organic/ferromagnetic nanoscale hybrids over distances of several nanometres thanks to their coupling to Skyrmions [37] on an underlayer.

A new perspective on the modulation of magnetic properties by molecular entities has been extended also to non-magnetic metals. Al Ma'Mari et al. [38] presented magnetometry and muon spectroscopy on Cu/C_{60} interfaces and provide conclusive evidence for the emergence of magnetism in multilayered planar structures. Thiol-coated Pt nanoparticles showed ferromagnetism above room temperature, and the coercive force was sensitively dependent on the molecular length and the particle size [39]. Such results open the way to the development of transformative classes of magnetic systems with potential applications in nanoscale sensors and memory devices [40].

In this brief overview of spinterface effects on the inorganic ferromagnetic side, the majority of the investigations refers to interface including 3d metals like Co or Fe. In spite of their large application in spintronic devices [41] the interaction between half metallic ferromagnetic oxides like La_{0.7}Sr_{0.3}MnO₃ (LSMO), Fe₃O₄ and CrO₂ or others and molecular compounds is relatively less investigated. Surface modeling of complex oxides [42] has to take into account of different termination layers and also has to include possible stoichiometric disorder. The number of possible adsorption configuration increases, making the predictive DFT activity quite consuming. Nevertheless, successful results have been obtained for benzene/LSMO [43] $C_{60}/LSMO$ [44] C_{60}/Fe_3O_4 [34]. Other interesting examples include the insertion of Cr_4O_5 layer at the $C_{60}/Fe(001)$ interface showing an unprecedented spin-polarization of the hybridized fullerene states.

2.2. Spinterface effects on molecular side

When an aromatic molecule is adsorbed on a FM surface, selective broadening of molecular orbitals and the formation of spin-split hybrid interface states take place. A very rich phenomenology has been found, including new substrate-mediated magnetic interactions, unprecedented chemical pathways for adsorbed organic molecules and exotic electronic and spin behavior [45]. The concept of spin-dependent hybridization at the ferromagnet/molecule interface and the corresponding formalism on the molecular orbitals has been clearly presented in Ref. [46]. We intend here to present a wide view of phenomena associated to modification of molecular states. An important effect is related to the so called spin filtering effect: non magnetic molecules can becomes spin active by acquiring spin polarization close to E_F and by acting as spin filtering element, making the spin polarization of a current injected across the interface be enhanced or even reversed with respect to the FM surface. This is the case of Tris-(8-hydroxyquinoline)aluminum (Alq₃)/Co interface investigated in Ref. [4] where unexpected positive spin polarization is detected in tunnel magnetoresistive device in contrast to the negative spin polarization of the bare Co film or the case of C₆H₆ on Fe₃O₄(001) where the molecular electronic states are spin-splitted, acting as molecular spin filtering elements [47]. Spin filtering effects via the device functionality, especially magnetoresistance, has been investigated in a number of different interfaces, namely Co/CoPc [48] where on symmetric devices Co/CoPc/Co inverse magnetoresistance was found contrary to the expected positive in reason of the device symmetry (same bottom and top Co/Pc interfaces). The inverse magnetoresistance in this case is associated to opposite spin polarization for the two interfaces, indicating how important is the metal-molecule contact geometry, presenting thus different coupling strengths when the molecule is deposited onto the metal or viceversa.

Several techniques have been used to detect and resolve the spin polarized states at interfaces. Spin-polarized scanning tunneling microscopy (SP-STM) is routinely used to map the spin density of states of molecules with atomic resolution as in the case of Pentacene ($C_{22}H_{14}$)/Co interface where reversed spin-polarization of molecular orbitals of Pentacene with respect to Co have been observed [49] or for H₂PC (hydrogen

ptalocyanine) on Fe showing a high, locally varying spin polarization ranging from attenuation to inversion with respect to that of the ferromagnetic Fe film [50]. Other examples include CoPc on Co [51] and CoPc and FePc on Fe [52]. SP-STM presents an extreme sensitivity of interface state formation and in particular to their relation with molecular electronic structure as in the case of Crq₃(Tris-(8-hydroxyquinoline)-Cr) and Alq₃(Tris-(8-hydroxyquinoline)-Al) [53] on Cr(001). In spite of their very similar frontier orbitals, a diverse range of spin-dependent interfacial coupling has been found each having distinct practical consequences for spin injection (see Fig. 3a,b,c,d). For the overall description of interfacial states, it is worth noting that not only the orbitals involved into the chemisorptions are fundamental but also molecular orbitals with geometrical extension far from the interface [30] because the spin polarized electronic configuration results from the overall computation of the DOS of the molecule and is then sensitive to small molecule changes [53].

An important class of organic materials widely investigated in this field is represented by metal organic complexes. The research was mainly stimulated by the idea to study the magnetic interactions of molecular magnetic ions with the substrate. In many planar molecules, such as metallic porphrines (Fig. 3e,f) or metal-phthalocyanine the orbital spatial extension favors the superposition with orbitals of the magnetic substrate. Based on elemental sensitivity, X ray magnetic circular dichroism (XMCD) measurements have been used to detect such correlations as in case of FePc on Co or even interaction mediated by interlayer as in case of oxidized surfaces [55,56]. Direct exchange correlate vanadylphthalocyanine (VOPc) deposited on ferromagnetic Fe, Co, and Ni films [57] while indirect exchange interaction between metal center and the substrate is mediated by orbitals in the surrounding, as for example the indirect exchange interaction of Fe in porphirines with Co atoms of the substrate mediated by the N orbitals of porphirine structure [58]. Here the distance between metal atoms is too large to promote the direct exchange interaction. With the same approach also single molecule magnet(SMM) and spin crossover have been investigated. Their geometrical conformation prevents the direct interaction between metal ions and the substrates, so typically the interaction take place via ligands as in case of antiferromagnetic coupling of Mn₁₂ on Ni mediated by S, C and O [59]. The ultimate goal of the application of SMM is to stabilize and increase their ordering temperature to higher values in order to extend their applicability to accessible cryogenic temperature. One of the aspect that are often neglected in studying the interfacial correlations is the dynamic of spin polarization at interfaces [60]: Spin-resolved pump-probe 2 Photon Photo-emission experiments has been used as for example in the



Fig. 3. (a,b,c,d) Top and lateral view of the Cr(001) surface upon the adsorption of $Alq_3(a,b)$ and $Crq_3(c,d)$ molecules, respectively. The dashed squares and the solid squares in (a,c) indicate respectively the unit cell and the surface atoms used for density of states analysis (blue and yellow colors in. (b,d)). Both molecules are quite similar and only differ for the metallic central ion but have different interfacial interactions with substrate and the electronic configuration is drastically different. Taken from Ref. [53] (e,f) Schematic representation of paramagnetic octaethylporphyrin molecule (e) and its spin configuration when absorbed onto Co layer. An antiferromagnetic order of the second ML is expected as schematized by the blue and red arrows in (f) Adapted from Ref. [54].

case of Co/Alq_3 interface [61] to study the dynamical spin relaxation of the long-living interface states [7]. In this case, the weak interaction with the second layer of the organic molecule pay an important role in the spin filtering effect, indicating that the interfacial effects are not strictly limited to the first molecular layer but extend over nm from the surface.

2.3. Spinterface effects on unconventional systems

The idea that molecular functionalisation is a way to tune the interaction involving only ferromagnetic ions is quite restrictive. The spinterface driving force is to introduce spin functionalities by interfacing functional systems with molecular entities. Successful results have been obtained with topological insulator: H₂Pc molecules bind strongly to topological insulator(TI) Bi2Se3 and introduce strong band bending effects and charge transfer into the TI, resulting in turn in the formation of the Rashba-split quantum-well states. Hybridization effects at the Bi₂Te₃/ MnPc interface have been used to achieve an efficient modification of the topological insulator [62]. On the other side, the decoration of a TI (SmB₆) surface with magnetic metallorganic clusters Cr₇Zn enable the scattering of electrons at the surface of the topological insulator demonstrating an effective method for modifying the TI surface properties [63]. These basic modifications are of extreme importance for integration of TIs into advanced device architectures, opening new and still unexplored avenues where the spin functionality of spin textured surfaces is tailored for spin-orbitronics applications [64]. Another class of materials that enter recently in the interest for spintronics are the 2D materials like graphene, silicene and transition metal dichalcogenides [65]. These compounds present very unusual physical characteristics, and have provided new platforms to probe the spin interactions [66]. The material's nature and the consequent importance of perturbation at the atomic site by surface ligands represents the driving force for the investigation in spintronics [67-69]. Also in this case the complexity of material interaction and their perturbation require a strong support from predictive activity.

3. Spinterface modulation

The ultimate goal of spinterface is to engineer and actively manipulate the hybridization layers to locate at the interface the functionalities that usually are encoded into bulk materials.

The most intuitive way to manipulate a spinterface is through a change in the bonding nature of the molecule and the surface [70]. Some of the most prominent examples have been already mentioned as for example the introduction of oxide interlayer [56] or a polar layer as LiF affecting the sign of MR in spin valve devices [71] or as tetracyanonaphtho-quinodimethane (TNAP) [72] where the reduction of the hole injection barrier induces an increase a spin carriers in organic spintronic devices. The chemical manipulation by substitution of molecule atoms has important effects on the overall electronic configuration as in the case of metal quinoline with different central ions [53] or in π conjugated system where some of the C atoms has been substituted with different electronegative ones [29]. Such examples nevertheless represent a "static" approach to manipulation of interfaces, where the hybridization is not more tunable. This limitation is overcome by profiting of the advantages of organic components thanks to their multifunctionality being able to respond to several stimuli also independently. Such aspects have been only marginally investigated in the field of spintronics, although they represents the most interesting aspect in spinterface science: the idea is to consider molecular hybrid interfaces as active elements able to translate input signal into various spintronic effects.

A possible way to realize the change of hybridization at interface is by external excitation, electrical, optical and even magnetic [82]. Organic components can be reactive to light and as in case of photoswitchable spin cross over where interconversion between spin (and so electronic) states occur with low power dissipation, high selectivity in picosecond scale upon light irradiation [73]. Once the molecular unit is selectively shined by light, its interaction with the ferromagnetic substrate can be modified and in turn the overall electronic and spin configuration at the interface. Spin crossover molecules are model systems for testing the manipulation of spin states: Jasper et al., [74] indicated that the spin state of molecules can be tuned by electrical methods via STM tip, each state having different coupling with the substrate. The use of electrical methods to control the spinterface is very appealing: one can figure out that excitation can be local and with limited energy transfer, able to respond to the electronics needs of low energy consumption and high density storage. The external electric field effect on the magnetism of C₆H₆-adsorbed Fe₃O₄(001) surface has been evaluated by density functional theory calculations demonstrating the possibility for electrically controlled magnetic data storage [75,76]. Attempts were conducted also with ferroelectric organic polymers [77,78]: the spin-polarization of the spinterface has been inverted by using PVDF-TrFE in contact with the ferromagnetic metal [79] in molecular tunnel junction by switching the polarization of the ferroelectric spacer. External control of spin polarization can be achieved by tuning the magnetoelectric properties of an ferroelectric/ferromagnetic interface. By switching the ferroelectric polarization state of a PbZr_{0.2}Ti_{0.8}O₃ (PZT) bottom layer within a PZT/Co/FePc-based device the magnetic properties of the interface with the organic layer is modified too [80]. Another important field of application for hybrizided interfaces is in magnetic storage. Reversible nonvolatile 180° magnetization switching is attracting increasing interest and exciting significant research activity in pure electric switching (the so called voltage controlled magnetization, VCM). In principle such effect can be obtained by tuning the hybridized states with specifically designed organic molecule surpassing the current limitation of screening effects in VCM [81] in reason of the extension of hybridized layers.

4. Conclusions

Organic molecules with their extreme flexibility and easy functionalization are really promising materials to design and control the functionalities of spintronics devices ultimately down to the interfacial layer scale. Hybridization at the interface between various organics and ferromagnetic metals leads to drastic changes of the properties of both layers, inducing modifications in the magnetic behavior of the ferromagnetic layer and, on the other hand, leading to spin polarized states in the molecular material, having dramatic effects on spin and charge injection. So far, the spin dependent electronic configuration of interfaces has been mainly investigated in linear approximation, considering a static bonding configuration, or in other words considering the interface as a passive element which spin configuration is nevertheless different from the corresponding bulk properties. The most recent understanding of spinterface indicate the possibility to move on nonlinear interfacial effects, via employing an active control of the hybridized layer via selective and tunable excitations such as light, electric field, or chemical doping. The interface could became thus an extraordinary tunable element in which the information can be stably encoded, providing innovative paradigms for future nanoelectronic solutions.

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