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The tunneling magnetoresistance and spin-polarized optoelectronic properties of graphyne-based molecular magnetic tunnel junctions

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Abstract

Using density functional theory and the non-equilibrium Green's function method, we investigate the spin-dependent transport and optoelectronic properties of the graphynebased molecular magnetic tunnel junctions (MMTJs). We find that these MMTJs exhibit an outstanding tunneling magnetoresistance (TMR) effect. The TMR value is as high as 10^6 %. When the magnetization directions of two electrodes are antiparallel under positive or negative bias voltages, two kinds of pure spin currents can be obtained in the systems. Furthermore, under the irradiation of infrared, visible or ultraviolet light, spin-polarized photocurrents can be generated in the MMTJs, but the corresponding microscopic mechanisms are different. More importantly, if the magnetization directions of two electrodes are antiparallel, the photocurrents with different spins are spatially separated, appearing at different electrodes. This phenomenon provides a new way to simultaneously generate two spin currents.

Keywords: tunneling magnetoresistance, molecular magnetic tunnel junction, optoelectronic properties, graphyne

(Some figures may appear in colour only in the online journal)

1. Introduction

Over the past few years, the magnetic tunnel junction (MTJ), as an important spintronic device, has aroused considerable interest owing to its importance in different application fields, such as magnetic sensors and magnetic random-access memory [1]. A basic MTJ is made of two ferromagnetic (FM) metal layers separated by a thin insulating (I) barrier layer; the structure can be formally expressed as FM/I/FM [2]. The insulating layer is so thin (a few nanometres or less) that electrons can tunnel through the barrier if a bias voltage is applied between the two FM metals. Various spin-dependent tunneling phenomena have been observed in MTJs and the most important property is that the resistance depends on the relative orientation of the magnetizations of the two FM metals. This phenomenon is called the tunneling magnetoresistance (TMR) effect [3]. In traditional MTJs, the FM metals are usually Fe, Co, Ni or related alloys while the insulators are typically MgO or Al₂O₃. Outstanding TMR effects have been observed in traditional MTJs [4–9]. For example, a TMR value of up to 604% at room temperature was observed in CoFeB/MgO/CoFeB MTJ [4]. Here TMR = $(R^A - R^P)/R^P$, where R^P (R^A) is the resistance when the magnetization directions of the two FM metal layers are parallel (antiparallel). The atomic-scale structure of CoFeB/MgO/CoFeB MTJ was then discussed [5]. In addition, Miyazaki *et al* demonstrated the possibility of large TMR values in MTJs with Al₂O₃ layers [6], and Moodera *et al* verified that at different temperatures, a notable TMR effect can be realized in CoFe/Al₂O₃/Co [7].

More recently, TMR in molecular magnetic tunnel junctions (MMTJs) has received much attention because, in these systems, quantum transport properties are dominant and can be chemically modified for better functionalities [10–14]. The appearance of graphene further promotes the progress of MMTJs [15–21], since in graphene the carriers hold a long mean free path, weak spin–orbit interaction and extraordinary mobility. For instance, Choudhardy *et al* reported the spin transport properties of B and N atoms doped CrO₂/graphene/CrO₂ [15]. They found that a large TMR value, 100%, can be obtained in the MMTJ. In another study [16], using zigzag graphene nanoribons (ZGNRs) and carbon chains, Deng *et al* designed various MMTJs and predicted a significant magnetoresistance effect.

Recently, it was shown that several graphene-like carbon allotropes can be stable and they widen the potential of lowdimensional carbon materials for applications [22, 23]. Of particular importance is so-called graphyne, which is a oneatom-thick carbon sheet, and is becoming a very interesting topic in the carbon material research community [24–26]. Different to graphene, graphyne contains both *sp* and *sp*² hybridized bonds, and holds four typical geometrical structures, i.e. α -, β -, γ - and (6, 6, 12)-graphyne. For these structures, only γ -graphyne is a semiconductor, while the other three are metals.

Although graphyne has been employed to construct various spintronic or molecular devices [27–29], its applications in MMTJ, compared with those of graphene, are still very limited. According to the above discussion, graphyne holds many unique physical and chemical properties, thus graphyne-based MMTJs may have richer transport properties. It will be interesting and necessary to explore the graphyne-based MMTJs. In the present study, we design different MMTJs using graphyne and discuss the transport properties. More specifically, in addition to traditional charge and spin transport, we further study the spin-polarized optoelectronic properties of the MMTJs. In fact, the spin-polarized optoelectronic properties of Fe-doped InP have been investigated very recently [30]. Novel spin-polarized optoelectronic phenomena could probably be found in the graphyne-based MMTJs.

2. Models and methods

The schematic structures of the graphyne-based MMTJs, M1 and M2, are shown in figure 1(a). Here we employed the γ -graphyne nanodot (γ GYND) as the 'insulating barrier layer'. Previous studies indicated that γ -graphyne is a semiconductor

[31, 32], and the corresponding band gap is about 0.5 eV. Our calculated results show that the energy gap of γ GYND is about 0.85 eV. Therefore, the energy gap of γ GYND is larger and can be viewed as an effective potential barrier.

Moreover, owing to the chemical similarity, the ZGNRs were chosen as 'FM metal electrodes'. Because the transport properties of the devices are dependent on the width of the ZGNR [21], we tested different ZGNR electrodes and finally designed M1 and M2. For different ZGNR electrodes, M1 and M2 have the best transport properties. In the two devices, through C–C bonds or sp^2 hybridized C atoms, the γ GYND is connected to ZGNRs, thus the contact structures of the two devices are different. To stabilize the systems, all the dangling bonds in the marginal C atoms are saturated by H atoms.

The two structures were fully optimized by using density functional theory (DFT) as implemented in the Atomistix ToolKit package [33]. The exchange–correlation functional was treated within the generalized gradient approximation proposed by Perdew, Burke and Ernzerhof (PBE) [34], and the double- ζ plus polarization (DZP) basis sets were adopted in the calculation. Careful and extensive convergence tests were performed. Finally, the kinetic cutoff energy was set to 200 Ry and, during the optimization, a criterion of 0.01 eV \AA^{-1} for atomic force was employed. The Brillouin zone was sampled by $1 \times 1 \times 100$ mesh points in k-space based on the Monkhorst-Pack scheme [35]. The 100 k-points were used to optimize the geometry structures of the devices and accurately calculate the transport properties. Along the x and y directions, a large vacuum space was included in the supercell to avoid interaction between the periodic images.

By combining the real-space non-equilibrium Green's function (NEGF) with DFT, the charge and spin transport behaviors of the MMTJs were studied. We firstly calculated the spin-polarized current I_{σ} at bias voltage $V_{\rm b}$ ($V_{\rm b} = V_{\rm L} - V_{\rm R}$, see figure 1(a)) according to the Landauer–Büttker formula [36]

$$I_{\sigma} = \frac{e}{h} \int T_{\sigma}(E) [f_{\rm L}(E) - f_{\rm R}(E)] dE$$
(1)

where $\sigma = \uparrow$ (spin up) or \downarrow (spin down), *e* is the electron charge, *h* is the Planck's constant, $T_{\sigma}(E)$ is the spin-resolved transmission spectrum and $f_{L(R)}(E)$ is the Fermi–Dirac distribution function for the left (right) electrode. Here $T_{\sigma}(E)$ was calculated by

$$T_{\sigma}(E) = \operatorname{Tr}[\Gamma^{\mathrm{L}}(E)G^{\mathrm{r}}(E)\Gamma^{\mathrm{R}}(E)G^{\mathrm{a}}(E)]_{\sigma\sigma}$$
(2)

where $\Gamma^{L(R)}(E)$ is the left (right) electrode self-energy function and $G^{r(a)}(E)$ is the retarded (advanced) Green's function.

In the MMTJs, the current under finite bias voltage is defined as

$$I^{\rm P} = I^{\rm P}_{\uparrow} + I^{\rm P}_{\downarrow} \text{ or } I^{\rm A} = I^{\rm A}_{\uparrow} + I^{\rm A}_{\downarrow}$$
(3)

where $I^{\rm P}$ and $I^{\rm A}$ are the total currents (the superscript 'P' or 'A' indicates whether the magnetization directions of the two electrodes are parallel or antiparallel), while $I_{\sigma}^{\rm P}$ or $I_{\sigma}^{\rm A}$ is the corresponding spin current calculated from equation (1). In addition, the total transmission coefficients could be expressed as $T^{\rm P}(E) = T_{\sigma}^{\rm P}(E) + T_{\sigma}^{\rm P}(E)$ or $T^{\rm A}(E) = T_{\sigma}^{\rm A}(E) + T_{\sigma}^{\rm A}(E)$

as $T^{P}(E) = T^{P}_{\uparrow}(E) + T^{P}_{\downarrow}(E)$ or $T^{A}(E) = T^{A}_{\uparrow}(E) + T^{A}_{\downarrow}(E)$. If $V_{b} \neq 0$ V, the spin polarization ratio of the current was calculated from



Figure 1. (a) The structures of the graphyne-based MMTJs. Blue bulks indicate the left and right electrodes, and V_L and V_R are the corresponding voltages. (b) The structures of the gate-controlled M1 and M2. Red bulks represent the left and right local gate electrodes, and V_{GL} and V_{GR} are the corresponding gate voltages. θ is the angle between the direction of light polarization and the *z* axis.

$$SP^{\rm P} = \frac{I^{\rm P}_{\uparrow} - I^{\rm P}_{\downarrow}}{I^{\rm P}_{\uparrow} + I^{\rm P}_{\downarrow}} \text{ or } SP^{\rm A} = \frac{I^{\rm A}_{\uparrow} - I^{\rm A}_{\downarrow}}{I^{\rm A}_{\uparrow} + I^{\rm A}_{\downarrow}}.$$
 (4)

As $V_{\rm b} = 0$ V, the above equations are simplified to $SP^{\rm P} = \frac{T_{\uparrow}^{\rm P}(E_{\rm F}) - T_{\downarrow}^{\rm P}(E_{\rm F})}{T_{\uparrow}^{\rm P}(E_{\rm F}) + T_{\downarrow}^{\rm P}(E_{\rm F})}$ or $SP^{\rm A} = \frac{T_{\uparrow}^{\rm A}(E_{\rm F}) - T_{\downarrow}^{\rm A}(E_{\rm F})}{T_{\uparrow}^{\rm A}(E_{\rm F}) + T_{\downarrow}^{\rm A}(E_{\rm F})}$, where $E_{\rm F}$ is the Fermi level. At zero or finite bias voltage, TMR is defined as [17]

$$TMR = \frac{T^{P}(E_{F}) - T^{A}(E_{F})}{T^{A}(E_{F})} \text{ or } TMR = \frac{I^{P} - I^{A}}{I^{A}}.$$
 (5)

Using the Nanodcal package [37], at the PBE/DZP level, we calculated the linear photocurrent I_{ph} according to the following formula [38]

$$I_{\rm ph} = \frac{{\rm i}e}{2\hbar} \int \frac{{\rm d}E}{2\pi} {\rm Tr} \{ [\Gamma^{\rm L}(E) - \Gamma^{\rm R}(E)] G^{<}(E) + [f_{\rm L}(E)\Gamma^{\rm L}(E) - f_{\rm R}(E)\Gamma^{\rm R}(E)] [G^{\rm r}(E) - G^{\rm a}(E)] \}$$
(6)

where $G^{<}(E)$ is the lesser Green's function. Since I_{ph} is proportional to the photon flux, accordingly, we can define the photoresponse function $f = I_{ph}/eF$ (*F* is the photon flux). Next we mainly focus on the photoresponse function *f*.

For the MMTJs, similar to equation (3), the f function can be written as

$$f^{\mathbf{P}} = f^{\mathbf{P}}_{\uparrow} + f^{\mathbf{P}}_{\downarrow} \text{ or } f^{\mathbf{A}} = f^{\mathbf{A}}_{\uparrow} + f^{\mathbf{A}}_{\downarrow}$$
(7)

where f_{σ}^{P} and f_{σ}^{A} represent the spin photoresponse functions.

It is worth noting that, for the incident photon, only the monochromatic plane wave was considered here. To produce a net photocurrent, a dipole potential is necessary for the photovoltaic process, which can be achieved by tuning the local gate voltage [38]. The structures of the gate-controlled M1 and M2 are given in figure 1(b). Two local gate electrodes are introduced in the system and the corresponding dipole potential $V_g = V_{GL} - V_{GR}$. In addition, the influence of light polarization on the optoelectronic properties was considered as well. Here, θ is used to represent the angle between the direction of light polarization and the *z* axis (see figure 1(b)). The photocurrent or photoresponse function will change with V_g and θ .

3. Results and discussion

3.1. The transport properties of the MMTJs under bias voltages

We will firstly discuss the transport properties of the MMTJs under finite bias voltages. The calculated spin densities, total currents and TMR curves are plotted in figure 2. It is obvious that the spin densities of the two devices are very similar. The magnetic moments of the ZGNRs mainly distribute at the edged carbons owing to the unsaturated π bonds, and the directions for the two sublattices are opposite. In contrast, the net spin on the γ GYND is very small and can be neglected. Such a magnetic structure could hold effective spin-dependent scattering [16], i.e. the transport properties of the electron depend on the spin.

For M1, at a low bias voltage ($|V_b| < 0.2$ V), the I^p and I^A curves have quite different trends. The former linearly increases with V_b while the latter is close to zero. Similar phenomenon is observed in M2 as well. The calculated results show that, for I^p , the differential conductances of the two devices at a very low bias voltage are constants and the corresponding values are 1.47 and 8.43 μ S, respectively. In other words, when the magnetization directions of the two ZGNRs are parallel, for small V_b the two devices can be viewed as classic resistors with different resistances.

A large difference between I^{P} and I^{A} causes an outstanding TMR effect at the small bias limit. As can be seen from figures 2(c) and (f), the maximal TMR values of M1 and M2 are $6.22 \times 10^{6}\%$ and $7.12 \times 10^{6}\%$, respectively, much larger than

those of other molecular devices [13–15, 20]. Meanwhile, such a large TMR effect can be kept for finite bias voltages $(|V_b| < 0.2 \text{ V})$. More importantly, although the contact structures in the devices are different, the TMR values hold the same order of magnitude, indicating that the TMR effect in the devices is robust, which is very important for constructing MMTJs [17]. Therefore, our results suggest that it is possible to design MMTJs using γ -graphyne, and the graphyne-based MMTJs have excellent transport properties. As $|V_b|$ gradually increases, the difference between I^P and I^A in M1 or M2 is limited; the TMR becomes smaller and smaller, and finally approaches zero.

To further analyze the transport properties of M1 and M2, the obtained spin currents are given in figure 3. If the magnetization directions of the two electrodes are parallel, the spin currents of M1 and M2 exhibit quite different trends (see figures 3(a) and (d)). For M1, although $I^{\rm P}_{\uparrow}$ and $I^{\rm P}_{\downarrow}$ are very close, the former gradually exceeds the latter when the bias voltage increases, i.e. $I_{\uparrow}^{\rm P} < I_{\perp}^{\rm P}$ as $|V_{\rm b}| < 0.4$ V but $I_{\uparrow}^{\rm P} > I_{\perp}^{\rm P}$ as $|V_{\rm b}| > 0.4$ V (the signs of $I^{\rm P}_{\uparrow}$ and $I^{\rm P}_{\downarrow}$ only represent the directions). As a result, the SP^{P} of M1 is small ($|SP^{P}| < 25\%$, see figure 3(c)) and changes its sign at about $|V_b| = 0.4$ V. For M2, interestingly, $I^{\rm P}_{\downarrow}$ is nearly zero in the whole bias region but $I^{\rm P}_{\uparrow}$ linearly increases and shows metallic behavior, leading to $I^{\rm P} \approx I^{\rm P}_{\uparrow}$. Accordingly, as shown in figure 3(f), the SP^{P} of M2 is always close to 100%, independent of the bias voltage. Thus M2 can be viewed as a perfect spin filter. The differences in the two devices suggest that the contact structure plays a role in the spin currents of the parallel case for the MMTJs.

To our surprise, when the magnetization directions of the two electrodes become antiparallel, M1 and M2 have very similar transport behaviors (see figures 3(b) and (e)). For the two devices, I_{\uparrow}^{A} monotonously increases in the negative bias region but is completely suppressed in the positive bias region, while I_{\downarrow}^{A} shows adverse behavior compared with I_{\uparrow}^{A} . In other words, $I^{A} \approx I_{\uparrow}^{A}$ as $V_{b} < 0$ V but $I^{A} \approx I_{\downarrow}^{A}$ as $V_{b} > 0$ V. In fact, the SP^{A} curves of the two devices are the same and both are step functions. This means that we can obtain two pure spin currents by changing V_{b} and that these models can act as dual spin diodes or dual spin filters; similar phenomena have also been observed previously [16, 20].

To understand the TMR effect and other spin-dependent transport properties of the devices, the transmission spectra and local device density of states (LDDOS) are given in figures 4 and 5. The LDDOS is a powerful tool to analyze the transport behaviors of the systems. Because LDDOS is dependent on the bias voltage V_b and energy E, here we give several typical results. For example, under a low bias voltage, only the LDDOSs at the Fermi level are given ($E = E_F = 0$ eV). For a high bias voltage, e.g. $V_b = 1.0$ V, the LDDOSs at the transmission peaks are presented.

At zero bias voltage, for M1, there are no effective transport channels at E_F for both parallel and antiparallel cases, and large gaps exist in the transmission spectra. Meanwhile, the related LDDOSs exhibit significant localized behaviors, indicating that it is difficult for the electrons to pass through



Figure 2. (a) The spin densities, (b) total currents and (c) TMR of M1. (d)–(f) are the related results of M2. In (a) and (d), red and blue represent net spin-up and spin-down components, respectively, and the isosurface value is taken as ± 0.005 e Å⁻³.

the device. As a result, the $T^{P}(E_{\rm F})$ and $T^{A}(E_{\rm F})$ of M1 are only 3.46×10^{-1} and 5.56×10^{-6} , respectively. Because at equilibrium the conductance is proportional to the transmission coefficient at $E_{\rm F}$ [36], it is not surprising that the TMR value is as high as $6.22 \times 10^{6}\%$. In fact, under low bias voltages, for M1 the transport channels of the antiparallel case are always blocked, leading to very small conductances and an outstanding TMR effect.

As for M2, in contrast to M1, the spin-up transport channels for the parallel case exist in the whole bias region, thus $I_{\uparrow}^{\rm P}$ linearly increases with $V_{\rm b}$. On the contrary, there are no effective spin-down transport channels as $V_{\rm b}$ changes from -1.0 to

1.0V. Accordingly, as shown in figure 4(c), at different bias voltages, the given spin-up LDDOSs are always delocalized while the spin-down components keep localized. Therefore, as mentioned before, M2 shows metallic behavior and $I^P \approx I_{\uparrow}^P$. When the magnetization directions of the two electrodes are antiparallel, under low bias voltages, similar to M1, all the transport channels in M2 are blocked and a significant TMR effect appears.

The spin currents in M1 and M2 could also be understood from figures 4 and 5. For example, from figure 5(a) we can see that for the two spins the transmission spectra and LDDOSs of V_b and $-V_b$ are opposite, i.e. the behavior of the spin-up



Figure 3. (a) and (b) The spin currents of M1. (c) The spin polarization ratio of the current in M1. (d)–(f) are the related results of M2.

electrons at V_b is the same as that of the spin-down electrons at $-V_b$, or vice versa. As a result, the spin-up and spin-down currents have the same trends under opposite bias voltages. Similar phenomenon has been observed in other magnetic devices [39]. To further confirm this, examples of the transmission eigenstates of M1 and M2 at given energies are shown in figure 6. We found that for the antiparallel case, the spinup and spin-down transmission eigenstates at V_b and $-V_b$ are indeed opposite. For example, when $V_b = -1.0$ V, for the two devices the spin-up transmission eigenstates are delocalized, while the spin-down components are localized. Therefore, under the negative bias voltages the spin-up current is dominant, and the SP^A is close to 100%. If V_b changes to 1.0V, we see that the spin-down current is preferable and SP^A is about -100%. In fact, such a dual spin-filter effect can also be understood from the electrodes' orbital symmetries [20].

According to the above discussions, the graphyne-based MMTJs have excellent transport properties. In the next section, we will discuss the spin-polarized optoelectronic properties of the devices.



Figure 4. (a) The transmission spectra of M1 and M2 when the magnetization directions of the two electrodes are parallel. The dashed lines indicate a bias window and $E_F = 0$ eV. (b) and (c) The local device density of states of M1 and M2 under different bias voltages. Red and blue represent spin-up and spin-down components, respectively, and the isosurface value is taken as 0.005 e Å⁻³.



Figure 5. Similar to figure 4 but for the antiparallel case.



Figure 6. (a) The transmission eigenstates of M1 at E = 0.49 eV for the antiparallel case ($|V_b| = 1.0 \text{ V}$). (b) The related results of M2 at E = 0.32 eV.

3.2. The spin-polarized optoelectronic properties of the MMTJs

Very recently, the optoelectronic properties of graphene and related optoelectronic devices have been carefully discussed [40]. Owing to their unique properties, graphene and related nanostructures have been employed to design various optoelectronic devices, such as a photodetector. Here we further investigated the spin-polarized optoelectronic properties of the graphyne-based MMTJs.

It is worth pointing out that, like our previous treatment [41], when different gate voltages are applied on the two gate electrodes (see figure 1(b)), an external potential drop is established across the device. Nevertheless, at $z = \pm \infty$, the system is not affected by the local gate voltages and the two electrodes still have the same chemical potentials. As a result, without photons, there is no net current; with photons, electrons may be excited from the occupied states to the unoccupied states and a net photocurrent will be generated by the dipole potential coming from the two gate voltages.

The calculated spin photoresponse functions are shown in figure 7. For M1, under the irradiation of infrared (IR), visible or ultraviolet (UV) light, f_{\uparrow}^{P} function always approaches zero.

On the contrary, f_{\downarrow}^{P} exhibits characteristic peaks at about 1 and 3.2 eV ($\theta = 0$) or 2.8 and 3.0 eV ($\theta = \pi/2$). As a result, by irradiating the IR or visible light of the given energies, we can directly excite the spin-down photocurrent from M1. As for M2, from figures 7(e) and (f) we see that non-zero f_{\uparrow}^{P} and f_{\downarrow}^{P} appear at about 0.1 eV ($\theta = 0$) and 4.8 eV ($\theta = \pi/2$) respectively, indicating that the spin photocurrent of M2 can be produced by IR or UV light and, in contrast with M1, both spin-up and spin-down photocurrents may be generated in M2. The differences in the two devices suggest that the contact structure also plays an important role in the spin-polarized optoelectronic properties.

The direction of the photocurrent varies with θ and the photon energy, namely the sign of the photocurrent depends on the two parameters. From a microscopic point of view, under light excitation the electrons transit from valence bands to conduction bands. If the conduction band curvatures are different for +k and -k (k is the point of the Brillouin zone), an imbalanced motion of excited electrons in the conduction bands occurs, which generates a photocurrent in the non-equilibrium situation. Depending on θ or the photon energy, the electrons are activated to different k-points in the



Figure 7. (a)–(d) The spin photoresponse functions of M1 under parallel and antiparallel cases as $\theta = 0$ or $\pi/2$ and $V_g = 0.01$ V. (e)–(h) are the related results of M2. a_0 is the Bohr radius.

conduction bands and acquire different band velocities. The sign of the photocurrent is determined by the summation of all the activated electrons with different distributions [42]. Therefore, the sign of the photocurrent varies for different θ and the incident photon energy.

The optoelectronic properties of the devices change dramatically with the magnetizations of the two electrodes. It is obvious that the behaviors of f_{σ}^{A} functions are quite different from those of f_{σ}^{P} functions. The calculated results show that f_{\uparrow}^{A} and f_{\downarrow}^{A} are the same; the only difference is that their directions are opposite. This phenomenon is very important because we can employ it to effectively separate two spins in space. For example, if the incident photon energy is about 1 eV and $\theta = 0$, in M1 f_{\uparrow}^{A} and f_{\downarrow}^{A} could reach about 14.5 and -14.5 a_{0}^{2} /photon, respectively (see figures 7(c) and (d)). As a result, the spin-up photocurrent appears in the right electrode and, at the same time, the spin-down photocurrent appears in the left electrode; the two spin photocurrents are spatially separated. Such a phenomenon is a new effect and undoubtedly differs from the situation under finite bias voltage, providing



Figure 8. (a) The spin-up photoresponse functions of M1 under the parallel case as $\theta = 0$ or $\pi/2$ and $V_g = 0.1$ V. (b) is the related result of M2.

a new way to simultaneously generate two spin currents. In addition, the photocurrents are enhanced in the antiparallel case. Generally speaking, the amplitude of f_{σ}^{A} is much larger than that of f_{σ}^{P} . This implies that the scatterings of photon-generated carriers in parallel and antiparallel cases are indeed different, and that not only the current but also the photocurrent could be controlled by changing the magnetizations of the electrodes.

Furthermore, we found that the microscopic mechanisms of the photocurrents excited by low-energy and high-energy photons are different. As an approximate estimation, the energy gap of the γ GYND is about 0.85 eV. The photons with energy larger than 0.85 eV will probably excite the electrons, in light of the optical selectivity rule, from the valence band to the conduction band or other empty bands. Then the electron-hole pairs will be separated by the local external potential V_{g} and finally form spin photocurrents through various spin-dependent scatterings. In contrast, we also observed that at a very low energy range, a non-zero photoresponse function still exists (see, for example, figure 7(e)). We suggest that this should be attributed to a kind of photon-assisted tunneling process, which is a typical quantum effect and has been carefully discussed in our previous study [41], i.e. with the assistance of low-energy photons, the tunneling probabilities of electrons become larger, which is beneficial for forming non-zero photocurrents.

In order to investigate the influence of V_g on the photocurrents, examples of the f_{\uparrow}^{P} functions of the devices when $V_g = 0.1$ V are provided in figure 8. It is obvious that the photocurrents are amplified as V_g changes from 0.01 to 0.1 V. Larger V_g results in the photon-generated carriers being more effectively separated, forming a larger photocurrent. More interestingly, a large external bias causes a photon-assisted tunneling process in M1 at the IR range when $\theta = 0$, and enhances such an effect in M2. Meanwhile, more peaks are formed in the visible and UV range and these peaks are influenced by θ . Therefore, by adjusting V_g and θ , we can obtain large light-generated spin currents from the graphyne-based MMTJs.

4. Conclusions

Using DFT and NEGF methods, we systematically investigated the transport and optoelectronic properties of graphynebased MMTJs. Our results suggest that these graphyne-based MMTJs have very large TMR effects, ~10⁶%. For the antiparallel case, nearly $\pm 100\%$ pure spin currents could be obtained at negative or positive V_b . In addition, spin photocurrents can be directly generated by irradiating these devices with IR, visible or UV light, but the corresponding microscopic mechanisms are different. More importantly, for the antiparallel case, the photocurrents with different spins are spatially separated, appearing at different electrodes. This phenomenon provides a new way to simultaneously generate two spin currents.

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