Can enhancement in tunnelling width influence the final spintronic feature of two-dimensional nanostructure of graphitic carbon nitride-(graphene)- graphitic carbon nitride?

Rinki Bhowmick, # Mausumi Chattopadhyaya† Jit Chakraborty, ## Barnadip Chakraborty††, Anusweta Roy††, Biswarup Neogi††, Sayantanu Koley### and Sabyasachi Sen#*

#Department of Physics, JIS College of Engineering, Block-A, Phase-III, Kalyani, Nadia PIN-741235, India

† Department of Chemistry, NIT-Calicut, Calicut Mukkam Road, Kattangal, Kerala 673601, India

†† Department of Electronics & Communication Engineering, JIS College of Engineering, Block-A, Phase-III, Kalyani, Nadia PIN-741235, India

### Department of Chemistry, JIS College of Engineering, Block-A, Phase-III, Kalyani, Nadia PIN-741235, India

#### Department of Chemistry, University of Calcutta, A.P.C. Ray Road, Kolkata-700 009, India

Email: sabyaphy12@gmail.com

Abstract. Herein we present a theoretical foray on crucial role played by the graphitic tunnelling barrier in tuning spintronic feature of two-dimensional insulating graphene layer sandwiched between two ferromagnetic graphitic carbon nitride (g- C₃N₃) electrodes. We mainly focused on the tuning of spin filter efficiency due to the alteration in tunnelling width. 100% spin filter efficiency reported at each tunnelling width. High degree of spin filter efficiency is restored even at finite bias over a wide range of bias range -1.0 V to +1.0 V. Entire observation have been explained by analysing transmission spectrum at zero bias and a molecular level origin of the observed spintronic response of the device have been provided by analysing the Molecular Projected Self-Consistent Hamiltonian states (MPSH) and transmission pathways of the system.
1. Introduction

In this ever-expanding research world one extremely popular but very recent invention is experimental realization of manipulating electron spin and designing novel devices out this. The spin state of electron can be controlled, detected and manipulated, and the subject of interest communally named as Spintronics. In recent times, Spintronics is in the major focus for the community of science in developing the performance of molecular electronic devices. High mobility of electrons, large spin relaxation time, capability of spin injection and less power dissipation are the main causes for the huge applications of spintronic devices in logic gates and quantum computing [1]. Recently, a number of pioneering theoretical as well as experimental research works suggest various aspects of spintronic action i.g. spin valve action, spin filtration action, spin switching and spin cross over action [2-6]. Among these spin filtration action gained one of the biggest attention due to its vast application in enhancing the performance of electronic devices.

Spin filter action is defined where one spin channel shows metallic behaviour keeping the other spin channel in the insulating state and this phenomenon is euphemistically known as half metallicity. Half metallicity has been reported in a number of literatures, e.g. in an Al/EuS/Au junction, Moodera et al.[6] observed high spin filtration action(90%) at 0.4 K. LeClair and their co-workers[7] reported high spin filter efficiency with TMR action in Al/EuS/Gd MTJ type device at 2 K. Also an experimental observation has been reported by Lüders et al. [8] in NiFe2O4 placed between two gold electrodes through counter electrode of La2/3Sr1/3MnO3. Recently Zhang et al.[9] reported 100% spin filter efficiency armchair graphene nanoribbons with a special edge hydrogenation (S-AGNRs). Also Pan and their co-workers[10] 100% spin filter efficiency in Mn- and Co-doped GyNRs at the fermi level.

A 2D graphene material has attracted a lot of attention due to its unique electrical as well as magnetic properties to enhance the properties of spintronic device[11]. Krasheninnikov et al., found strong bonding and calculated magnetic moment for transition-metal atoms when embedded in a graphene sheet [12]. Dmitry and their co-workers has reported spin-filtered edge states in Graphene[13]. Pandey et al. found spin filtration action in functionalized graphene sheet placed between CrO2 as electrode [14]. Besides that, in a recent literature Sen et al. reported graphitic carbon nitride (g-C4N3) as a potential half metallic material [15].

With this back ground we have selected a 2D graphene sheet placed between two g-C4N3 electrodes, where the graphene sheet acts as insulator having zero band gap. We calculated the current-voltage characteristics of the complex systems with altering the tunnel width within a bias range of -1.0 V to +1.0 V. While chosing different width of graphene we calculated spin filter efficiency(SFE) at zero bias and Bias dependent spin injection coefficient (BDSIC) at different bias. The observed 100% SFE for all different tunnel/insulating width dictates g- C4N3 as a propitious candidate for spintronic device. This superlative observation has been explained by analysing transmission spectrum, transmission pathways and MPSH states of the proposed devices.

2. Computational Details

To start with the present investigation, first we optimized g-C4N3unit using Gaussian16 suite of programme within the framework of density functional theory using hybrid B3LYP functional [15,16]. Quickly after optimization we placed 2D graphene of different width one by one two g-
C4N3 electrodes and re-optimized each of them separately using double zeta polarized (DZP) basis set and PBE functional using ATK2019.12 [17] program. We performed all quantum transport related calculation by exploiting Green’s function (NEGF) formalism fixed with density functional theory (DFT) and using Perdew-Burke-Ernzerhof (PBE) [18] type GGA functional combined with DZP basis set. The quantum transport parameters were estimated with core electrons defined by norm-conserving Troullier–Martins pseudopotentials [19]. In the direction of transport 100 k points and 150 Ry cut off energy were used to evaluate some relevant parameters for self consistent field (SCF) analysis. Up and down spin current are evaluated using Landauer and Büttiker formula [19-21] as given below:

\[
I(\phi) = e \sum_{\sigma} \int_{\mu_{L}}^{\mu_{R}} T_{\sigma}(E, \phi) \left[ f_{L}(E - \mu_{L}) - f_{R}(E - \mu_{R}) \right] dE
\]

Here, \(T_{\sigma}(E, \phi)\) signifies the spin-dependent transmission coefficient and \(f_{L(R)}\) denotes the Fermi function of the left and right electrode and can be represented as

\[
f_{L(R)}(E) = \frac{1}{1 + \exp[(E - \mu_{L(R)})/kT]}
\]

Now \(\mu_{L(R)}\), \(k\) and \(T\) have their usual meaning as chemical potential of electrodes, Boltzmann constant and temperature, respectively. The chemical potential is further defined as \(\mu_{L(R)} = E_{F} \pm \frac{e\phi}{2}\) where \(E_{F}\) is the Fermi energy of the electrode(s).

3. Results and Discussions

Figure 1 represents two-probe optimized structure of 2D nanostructure of g-C₄N₃-gr-g-C₄N₃ where g-C₄N₃ electrodes is in its ferromagnetic state. The particular reason of choosing ferromagnetic electrodes is lies behind the fact that ferromagnetic state of g-C₄N₃ is more stable than its non-magnetic and anti-ferromagnetic counter parts as reported by Du et al. [22]. Particularly the ferromagnetic state of g-C₄N₃ is more stable than AFM and NM states by an amount of 0.25 and 0.23 eV, respectively.

Current – Voltage (I-V) Characteristics

To begin with our study, we chose five different widths of 2D graphene: 22.36 Å, 31.96 Å, 36.69 Å, 51.58 Å and 63.73 Å, respectively. The corresponding I-V plots are given in Fig. 2(a) and 2(b). A meticulous inspection of the figures reveal the fact that the highest current density obtained at the minimal width (22.36 Å) of graphene (insulating barrier) and decreasing gradually with increasing the width of the insulating spacer from 31.96 Å to 63.73 Å. The second important feature of the I-V plots is that in all cases the current is contributing mainly by the down spin channel keeping the up spin in the insulating state. We have discussed spin filter action in the following sections.
Fig. 2. Bias dependence of spin polarized current (in nA) in 2D nanostructure of g-C$_4$N$_3$-gr-g-C$_4$N$_3$ obtained at tunnelling width of (a) 22.36 Å (b) 31.96 Å, 36.69 Å, 51.58 Å, 63.73 Å respectively.

**Spin Filter Efficiency (SFE)**

As clearly evident from Fig.2 g-C$_4$N$_3$-gr-g-C$_4$N$_3$ acts as a spin filter irrespective of the width of the mediated graphene unit. In general spin filter action is quantified by calculating the spin filter efficiency using the following formula:
\[
SFE = \frac{T_{\uparrow}(E_F) - T_{\downarrow}(E_F)}{T_{\uparrow}(E_F) + T_{\downarrow}(E_F)} \times 100\% \tag{2}
\]

Where, \(T_{\uparrow}(E_F)\) and \(T_{\downarrow}(E_F)\) characterize the transmission coefficient of the up and down spin channels. Using this equation (2) we have calculated the SFE for g-C\(_{4}N_3\)-gr- g-C\(_{4}N_3\) altering the width of graphene 22.36, 31.96, 36.69, 51.58 and 63.73Å, respectively. In each case we found that g-C\(_{4}N_3\)-gr- g-C\(_{4}N_3\) shows 100% SFE irrespective of the width of graphene sheet (see Fig. 3(a)).

Fig. 3. Tunnelling width dependence of spin filter efficiency in 2D nanostructure of g-C\(_{4}N_3\)-gr- g-C\(_{4}N_3\)

**Bias Dependent Spin Injection Coefficient (BDSIC)**

Next, in this order to explore the spin filter efficiency at finite bias we have performed bias dependent spin injection coefficient by using the formula given as

\[
\eta = \frac{I_{\text{spin-up}} - I_{\text{spin-down}}}{I_{\text{spin-up}} + I_{\text{spin-down}}} \tag{3}
\]

where, \(I_{\text{spin-up}}\) and \(I_{\text{spin-down}}\) denotes the up and down spin currents, respectively. The value of BDSIC has been plotted against applied bias and the plotted graph is given by Fig. 3 which clearly demonstrates constant values of BDSIC i.e. 100% over the complete bias range from -1.0 V to +1.0 V.
across the entire range of variation of tunnelling width from 22.36 to 63.73 Å. This feature is well manifested in Fig. 3b and of course provides a powerful evidence of g-C₃N₄-gr-g-C₃N₄ as a robust spin filter material.

**Analysis of transmission spectrum at zero bias**

To examine the origin of such high spin filter efficiency, we have analysed transmission spectrum at zero bias and the corresponding results is presented in Fig. 4(a) and 4(b). A close inspection of Fig. 4a) clearly demonstrates high transmission coefficient at the Fermi level for down spin channel compare to up spin channel where the width of the graphene is of 22.36 Å. However, the value of transmission coefficient is comparatively low for other cases where the width of the graphene units is chosen as 31.96, 36.69, 51.58 and 63.73 Å respectively. The zero bias transmission spectrum corroborates and explains all the I-V plot shown in Fig 2.
Analysis of Transmission Pathways

In this section we have evaluated the impact of quantum mechanical effect on high spin filter efficiency of g-C_4N_3-gr- g-C_4N_3. Analysis of transmission pathways is one of the possible way to check how the current of up and down spin channel are effected by the quantum interference of electrons. The zero bias transmission pathways for g-C_4N_3-gr- g-C_4N_3 at a width of 22.36 Å graphene is provided in Fig. 5. The phase of transmission pathway vector is signified by blue, green and red arrows and the direction of these arrows specifies the direction of current (i.e. flow of electrons). Importantly there are three phases to specify: ‘zero phase or in phase’, ‘π/2 phase or out of phase’ and ‘π phase or opposite phase’. Presence of large number of blue arrows indicate constructive interference which reflects in the increased of resultant current density. However, presence of green and red arrows result destructive interference and causes decrease of resultant current. Fig. 5 (a) represents the transmission pathways of g-C_4N_3-gr- g-C_4N_3 at graphene width of 22.36 Å, where the transmission vector is absolutely absent for up spin channel. On the contrary, in Fig. 5(b) presence of large number of blue arrows causes destructive interference for spin down channel. The transmission pathways in Fig 5(a) and (b) therefore clearly explains the I-V plot given in Fig 2 i.e. the insulating nature of the up spin and metallic nature of down spin channel of g-C_4N_3-gr- g-C_4N_3 at a graphene width of 22.36 Å and hence the high current density vis-à-vis the 100% spin filter action. It is worth to mention that the figures 5(c) – (j) display the transmission pathways of g-C4N3-gr-g-C4N3 considering the width of graphene 31.96 Å, 36.69Å, 51.58 Å and 63.73 Å, respectively. In all of these figures absence of transmission pathway vectors support the insulating nature of up spin channels and hence low current density as shown in Fig 2(b). However, in the Fig 4(d), (f), (h) and (j) the presence of large number of red and green arrows from the down spin channels dominated the destructive interference and reduce the current density of g-C_4N_3-gr- g-C_4N_3 (see Fig 2) compare to the one where the smallest width (22.36 Å) of graphene is considered.
3.4 Analysis of Molecular Projected Self-Consistent Hamiltonian (MPSH)

Finally, to dig out the origin of high SFE in terms of molecular level, we analysed the molecular projected self-consistent Hamiltonian (MPSH) states of g-C$_4$N$_3$-gr- g-C$_4$N$_3$ for above five different lengths from 22.36 Å to 63.73 Å. The specific matrix for each eigen state called MPSH state which is formed due to L-C-R interaction and the corresponding expression is given as:

$$
\begin{bmatrix}
H_L + \Sigma_L & V_L & 0 \\
V_L^\dagger & H_C & V_R \\
0 & V_R^\dagger & H_R + \Sigma_R 
\end{bmatrix}
$$

Where L, R and C denotes to left electrode, right electrode and central region of the two probe configurations. Here, $H_{(L,R)}$, $H_C$ and $H_{(C)}$ are the Hamiltonian matrices in the left electrode (L), right electrode (R), contact region (C), respectively, and the interaction potentials between L-C and L-R regions are characterized by $V_L$ and $V_R$, respectively. Fig. 6(a) & 6(b) demonstrate the MPSH states of g-C$_4$N$_3$-gr- g-C$_4$N$_3$ for up and down spin channels considering the tunnelling width (i.e. graphene) of 22.36 Å. A close view at the figures manifest that the down spin electrons are much more delocalized compare to the up spin electrons which is a direct evident come explanation of the high current density obtained from the up spin channel. The corresponding MPSH states of up and down spin channels of g-C$_4$N$_3$-gr- g-C$_4$N$_3$ at all others width (namely 31.96, 36.69, 51.58 and 63.73 Å) are presented in Fig 6(c)-(j) respectively.
Fig. 6 MPSH states in 2D nanostructure of g-C₃N₄-gr-g-C₃N₄ attained at tunnelling width of 22.36 Å at (a) & (b), 31.96 Å at (c) & (d), 36.69 Å at (e) & (f), 51.58 Å at (g) & (h), 63.73 Å at (i) & (j) respectively.

4. Conclusions
In conclusion, we have shown that g-C₃N₄-gr-g-C₃N₄ can act as a perfect spin filter irrespective of the width of the tunnelling barrier, graphene. The spin filter action is featured from the downspin channel keeping the up spin in insulating state. However, the high current density obtained only while choosing a critical width of graphene as 22.36 Å. With increasing the width of the insulating tunnel barrier, graphene, the current density diminishes sharply. The spin filter action, insulating nature of the up spin channel electrons of g-C₃N₄-gr-g-C₃N₄ have been analysed and explained in terms of transmission spectrum, transmission pathways and MPSH state analysis. Our investigation exclusively proofs g-C₃N₄-gr-g-C₃N₄ as a perfect spin filter.

Financial Support:
All India Council of Technical Education (AICTE), Govt. of India for the research funding [Ref. No.: File No. 8 – 18/RIFD/RPS/POLICY-t / 2016 – 17 Date: 14 September 2017] and DST-FIST project [SR/FST/COLEGE/-2017/127 Order issued 27th August 2018]. SERB (Science and Engineering Research Board) for funding through TARE (Teachers Associateship for Research Excellence) scheme.

Acknowledgements:
SS acknowledges All India Council of Technical Education (AICTE), Govt. of India for the research funding [Ref. No.: File No. 8 – 18/RIFD/RPS/POLICY-t / 2016 – 17 Date: 14 September 2017] and DST-FIST project [SR/FST/COLEGE/-2017/127 Order issued 27th August 2018]. MC thanks SERB (Science and Engineering Research Board) for funding through TARE (Teachers Associateship for Research Excellence) scheme.

Reference:
[1] Kim W Y and Kim K S 2008Nat. Nanotechnol.3 408
[2] Nguyen T D, EhrenfreundE and Vardeny Z V2012 Science337 204-209
[3] A Fert, 2008Rev. Mod. Phys.80 1517
[4] Sen S and Chakrabarti S2010 J. Am. Chem. Soc.132 15334
[5] Sen S and Chakrabarti S 2014Chem. Phys. Chem.152756.
[6] Weymann I and Barna’s J 2008Appl. Phys. Lett.92103127
[7] Moodera J S, HaoX, GibsonG A and MeserveyR 1988 Phys. Rev. Lett.61 637
[8] LeClairP, Ha J,SwagtenJ M,KohlheppJ T, van de Vin C H and de Jonge W J M, 2002Appl. Phys. Lett.80 625
[9] Zhang D, Long M, Zhang X, Cui L, Li X and HXu2017J. App. Phys.121 093903
[10] Pan J, Du S, Zhang Y, Pan L, Zhang Y, Gao H-Z and PantelidesS T 2015 Phys. Rev. B92205429.
[11] Geim A Kand NovoselovK S 2007 Nat. Mater.6183
[12] Krasheninnikov A V, Lehtinen P O, Foster A S, Pyykkö P and Nieminen R M 2009 Phys. Rev. Lett.102 126807
[13] DmitryAA, LeeP A and L S Levitov2006 Phys. Rev. Lett.96 176803
[14] Pandey N, KumarA and Chakrabarti S2020 J. Magn. Magn. Mater. 497 166073.
[15] BeckeA D 1993 J. Chem. Phys.98 1372
[16] LeeC, YangW and ParrR G1988 Phys. Rev. B 37 785
[17] www.quantumwise.com
[18] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[19] Datta S 1995 Electronic Transport in Mesoscopic Systems, Oxford University Press, New York.
[20] Zhu Z G, Su G, Zheng Q R and Jin B 2002 Phys. Lett. A300 658
[21] Zhu Z G, Su G, Zheng Q R and Jin B 2004 Phys. Rev. B70 174403
[22] Du A, Sanvito S, Li Z, Wang D, Jiao Y, Liao T and Smith S C 2012 J. Am. Chem. Soc. 1344393