Lower Electric Field Driven Magnetic Phase Transition and Perfect Spin Filtering in Graphene Nanoribbons by Edge Functionalization

M. Reza Rezapour, [†‡] *Jeonghun Yun,* [†‡] *Geunsik Lee,* [‡*] *and Kwang S. Kim* [†‡*]

[†]Center for Superfunctional Materials, [‡]Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Korea.

[*] gslee@unist.ac.kr , kimks@unist.ac.kr

Supporting Information

Hamiltonian for the mean field π orbital Hubbard model is given below.

$$H = t \sum_{\sigma,<i,j>} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} + \sum_{i} V_i c_{i\sigma}^{\dagger} c_{i\sigma}$$

The hopping parameter t and on-site Coulomb repulsion U are chosen as t = -2.77 eV, U = 2.7 eV. The last term describes the on-site energy level which is equal to zero for the zero transverse electric field or symmetric functionalization of two edges. For non-zero transverse electric field *E* or in the presence of electron-donating/withdrawal groups at opposite edges, V_i is varied to be non-zero only for edge atoms as $+V_0$ and $-V_0$, respectively, where $V_0 = EW/2$ with W being zGNR width. It means external potential is steeply screened. Figure S1 represents the calculated band structures E(k) and local density of states (LDOS) of two edge carbon atoms (C1 and C2) at the opposite edges of zGNR for four different transverse electric fields denoted by V_0 = 0.0, 0.30, 0.356, 0.50 V. At zero electric field (V_0 = 0.0 V) the up and down spin states are degenerate in the vicinity of Fermi level. Increasing electric field (V_0 = 0.30 V) breaks the symmetry of LDOS on the edge atoms and the degeneracy of the spin states near the Fermi level is removed. At V_0 = 0.356 V, LDOSs for up spin on edge carbon atoms have overlap and consequently the system exhibits half metallicity. Increasing electric field further (V_0 = 0.50 V) eventually makes the population of spin up and down electrons equal on all carbon atoms and the system becomes nonmagnetic.

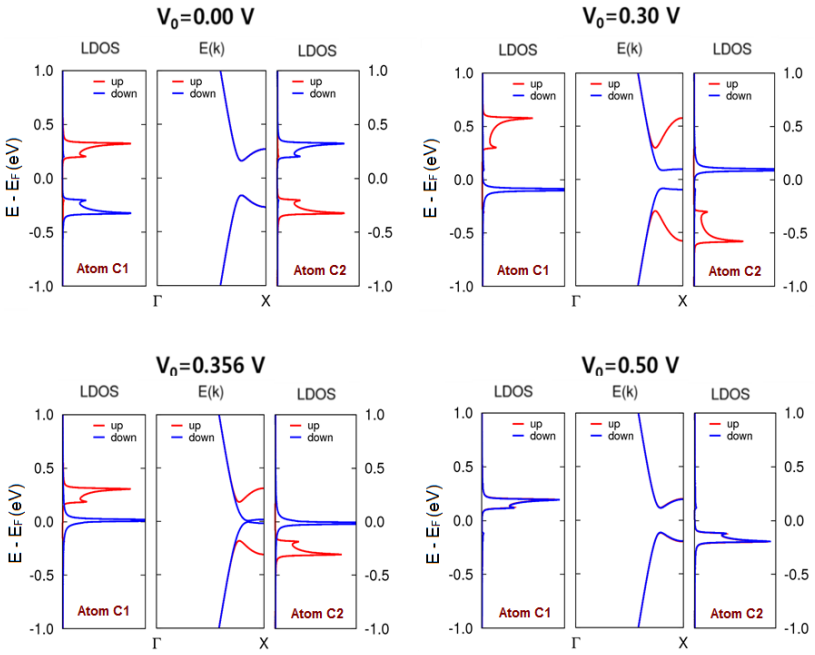

Figure S1. Local density of states and band structure of two edge carbon atoms of pristine 8-zGNR for four different transverse electric fields denoted by V_0.

We employ the above mentioned Hamiltonian to investigate the population of spin up and spin down electrons on each carbon atom of the system. It is explicitly shown (Figure S2) that by increasing external transverse electric field (V_0 = 0.30 V and 0.356 V) the population of spin up electrons on one edge carbon atom (C1) decreases while it increases on the opposite edge carbon atom (C2). Finally at certain critical electric field (V_0 = 0.50 V) the populations of electrons with up or down spin on each carbon atom become equal which denotes that the system shows nonmagnetic behavior. Figure S3 illustrates the variation of the total number of electrons on each carbon atom in terms of applied electric field.

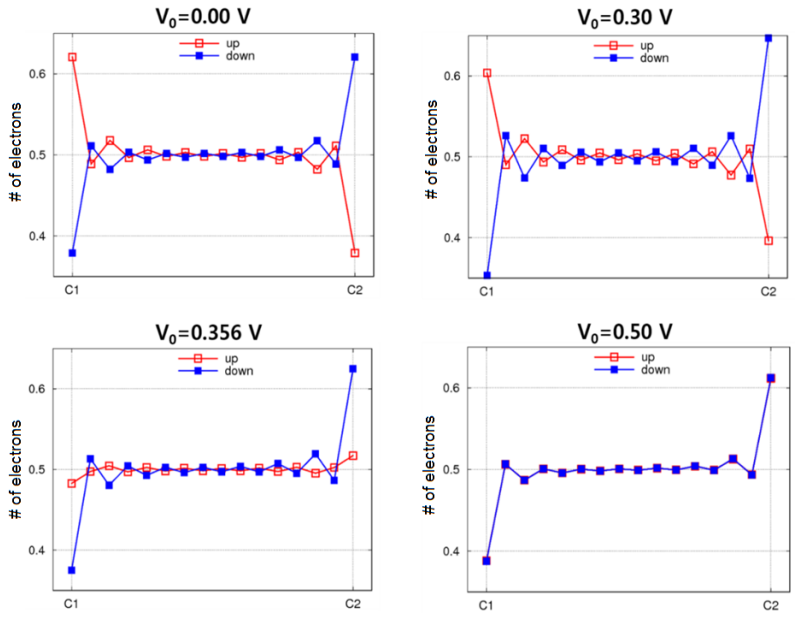

Figure S2. The number of spin up and down electrons at each carbon atom along the width of zGNR.

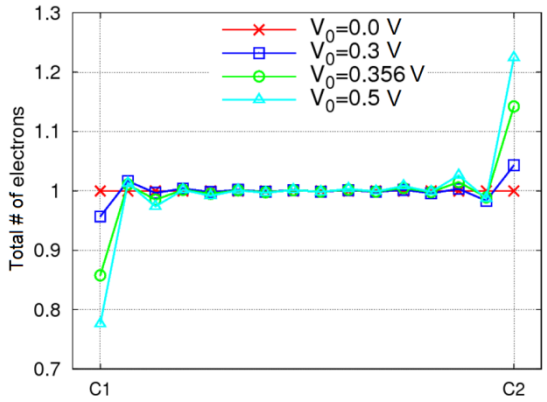

Figure S3. Total number of electrons at each carbon atom along the transverse direction of zGNR.

To study the effect of density of functional groups on the critical electric field (*Ec*) to obtain nonmagnetic zGNR, we replace hydrogen atoms on the edge of pristine 8-zGNR by functional groups in the order of 1/N where N-1 represents the number of edge-passivating hydrogen atoms between two nearest functional groups. Figure S4(a) shows the variation of *Ec* for 8-zGNR modified by O-H/C-N groups where the covered length of the edges changes from 1/2 to 1/8. O-H and C-N groups are located in front of each other; however, our calculations show that moving one of the groups to the neighbor site does not change the corresponding *Ec* value provided the order of functionalization is preserved.

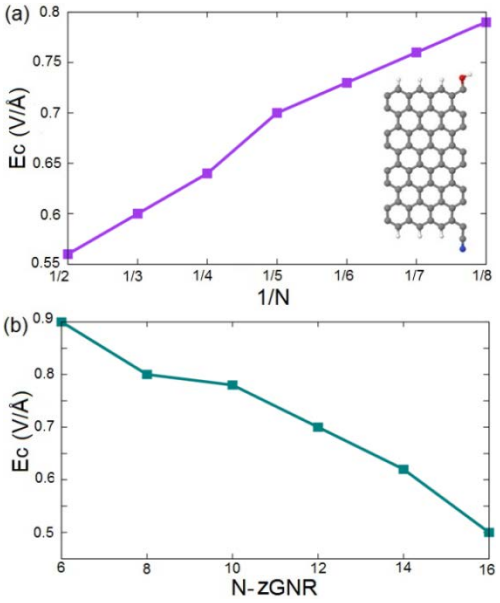

Figure S4. Variations of critical electric field (*Ec*) in terms of (a) coverage fraction of zGNR edges by O-H/C-N groups and (b) width of pristine zGNR. The inset in (a) shows edge modified 8-zGNR with the coverage fraction of 1/4.

It is shown that by decreasing the concentration of the functional groups on the edges, the *Ec* value increases almost linearly. It is expectable because decreasing the number of functional groups on the unit length of the zGNR edge reduces the potential difference between two edges. However the necessary electric field to obtain nonmagnetic zGNR is still lower than that for pristine zGNR even when the coverage fraction is 1/7.

The other factor which influences the magnitude of *Ec* is the width of zGNR. To investigate the effect of width of zGNR on the values of *Ec*, we consider 6, 8, 10, 12, 14 and 16-zGNRs and calculate the critical electric field in each case. The obtained values are illustrated in Figure S4(b). It is observed that increasing the width of zGNR diminishes *Ec*. The reason is that the electrostatic potential difference between the two edges is proportional to the system size for a given value of the transverse electric field. Similar to the diminution of *Ec* by decreasing the fraction of functional groups, the reduction in *Ec* due to increasing the width of zGNR is almost linear.