Support Information

Transport Properties of Zigzag Graphene Nanoribbons Decorated by Carboxyl Group Chains

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Reference numbers are those in the manuscript.

The dependence of the transport properties of 9ZGNR-3OH and 9ZGNR-5OH on the decorated position

To represent the dependence of the transport properties of 9ZGNR-mOH on the decorated position, we take 9ZGNR-3OH and 9ZGBR-5OH as the typical examples and study their transport properties as the decorated position is gradually moved to the edge of the ribbon. Such systems are denoted as N_1C-mOH-N_2C, where m is the number of oxidized carbon chains, N_1 and N_2 denote the number of un-oxidized zigzag carbon chains remaining graphene structure on two sides of the decorated position, respectively. Figure S1 shows the dependence of the transmission conductance of 9ZGNR-3OH and 9ZGNR-5OH on the OH decorated position. We find that the transmission conductance around the Fermi level of 9ZGNR-3OH and 9ZGNR-5OH is sensitive to the OH decorated position. The 6 G_0 transmission plateau of 9ZGNR-3OH is depressed gradually with the movement of decorated position from the center to the edge. However, the transmission conductance within the energy window [-0.9eV, 1.5eV] still remains $2G_0$ for 2C-3OH-4C and 1C-3OH-5C. Especially, there is a $3G_0$ plateau within the energy window [-0.25eV, 0.25eV] for 2C-3OH-4C, as shown in Figure S1. The transport properties of 9ZGNR-3OH are still enhanced in comparison with those of pristine 9ZGNR except for 3OH-6C. Interestingly, as for 3OH-6C (the OH decorated and un-decorated region are phase separated), the transmission conductance around the Fermi level([-1.0eV, 1.0eV]) is similar to that of pristine ZGNRs. Namely, sp^2 graphene region of phase separated 9ZGNR-3OH behaves as pristine graphene nanoribbon, which is similar to the case of graphane-graphene hybrid nanoribbons.[16,35,36] As for 9ZGNR-5OH, the semi-conductive 2C-5OH-2C transforms into metal when the decorated position deflects from the center. The transmission conductance of 1C-5OH-3C shows $2G_0$ to $3G_0$ plateaus when the energy is larger than -1.25 eV. Similarly, the transmission conductance of 5OH-4C (phase separated system) behaves as pristine graphene nanoribbon around the Fermi level.

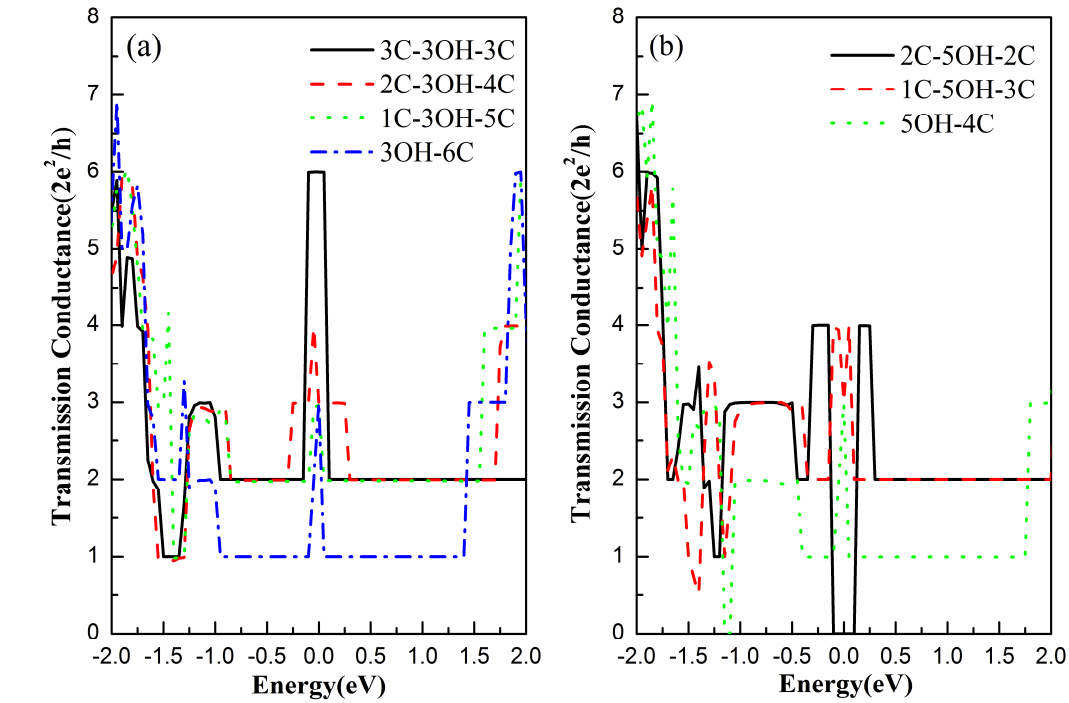
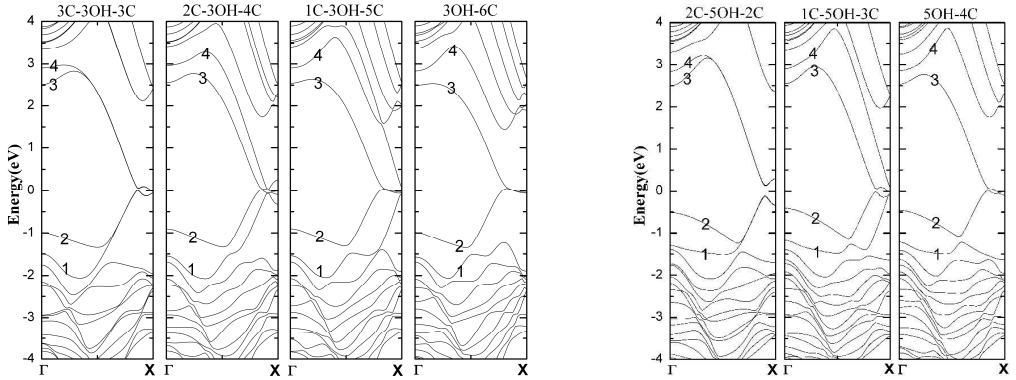


Figure S1: Transmission spectra of (a) 9ZGNR-3OH and (b) 9ZGNR-5OH with different OH decorated position.

To investigate the mechanism of the metal-semiconductor transition of 9ZGNR-mOH and the dependence of the transport properties of 9ZGNR-mOH on the decorated position, we calculate the band structures and the charge density distributions corresponding to the bands around the Fermi level of 9ZGNR-3OH and 9ZGBR-5OH, as shown in Figure S2 and Figure S3. The dependence of the transport properties of 9ZGNR-mOH on the decorated position derives from the energy shift of the second highest valence band (SHVB), VBM, CBM and second lowest conduction band (SLCB) induced by the movement of the decorated position. The results of the band structures and the charge density of 9ZGNR-3OH and 9ZGNR-5OH depending on the OH decorated position indicate that the un-decorated graphene regions determine the transport properties of the systems. When 9ZGNR-H is decorated by the OH chains at the center of the ribbon, two un-decorated graphene regions are introduced. The bands near the Fermi level mainly derive from these un-decorated

graphene regions as shown in Figure S3. When both un-decorated graphene regions are wider than 2 zigzag chains, such as 3C-3OH-3C, the two un-decorated graphene regions and the decorated region contribute to the VBM and SHVB and the two un-decorated graphene regions contribute to the CBM and SLCB around the Fermi level. Such four bands overlap around the Fermi level resulting in the enhancement of their transmission conductance. When the width of one of the two un-decorated graphene regions is smaller than 3, such as 1C-5OH-3C of 9ZGNR-5OH and the 1C-3OH-5C and 2C-3OH-4C of 9ZGNR-3OH, the SHVB and SLCB mainly derive from the narrower graphene region while the VBM and CBM mainly derive from wider graphene region. Peierls distortion[34] in such narrow graphene region (neighboring π electrons form dimers in the same zigzag chain as shown in Figure S3) induces the energy opposite shift of the SHVB and SLCB resulting in the separation of these two bands around the Fermi level. The depression of the transmission conductance enhancement of 2C-3OH-4C and 1C-3OH-5C originates from the separation of the SHVB and SLCB. When both un-decorated graphene regions are smaller than 3 zigzag chains, such as 2C-5OH-2C, the VBM and CBM also separate from each other resulting in the transition from metals to semiconductors.



(a) (b)

Figure S2: Band structures of (a) 9ZGNR-3OH and (b) ZGNR-5OH with different OH decorated position. The number, 1, 2, 3 and 4 denote the SHVM, VBM, CBM and SLCM, respectively.

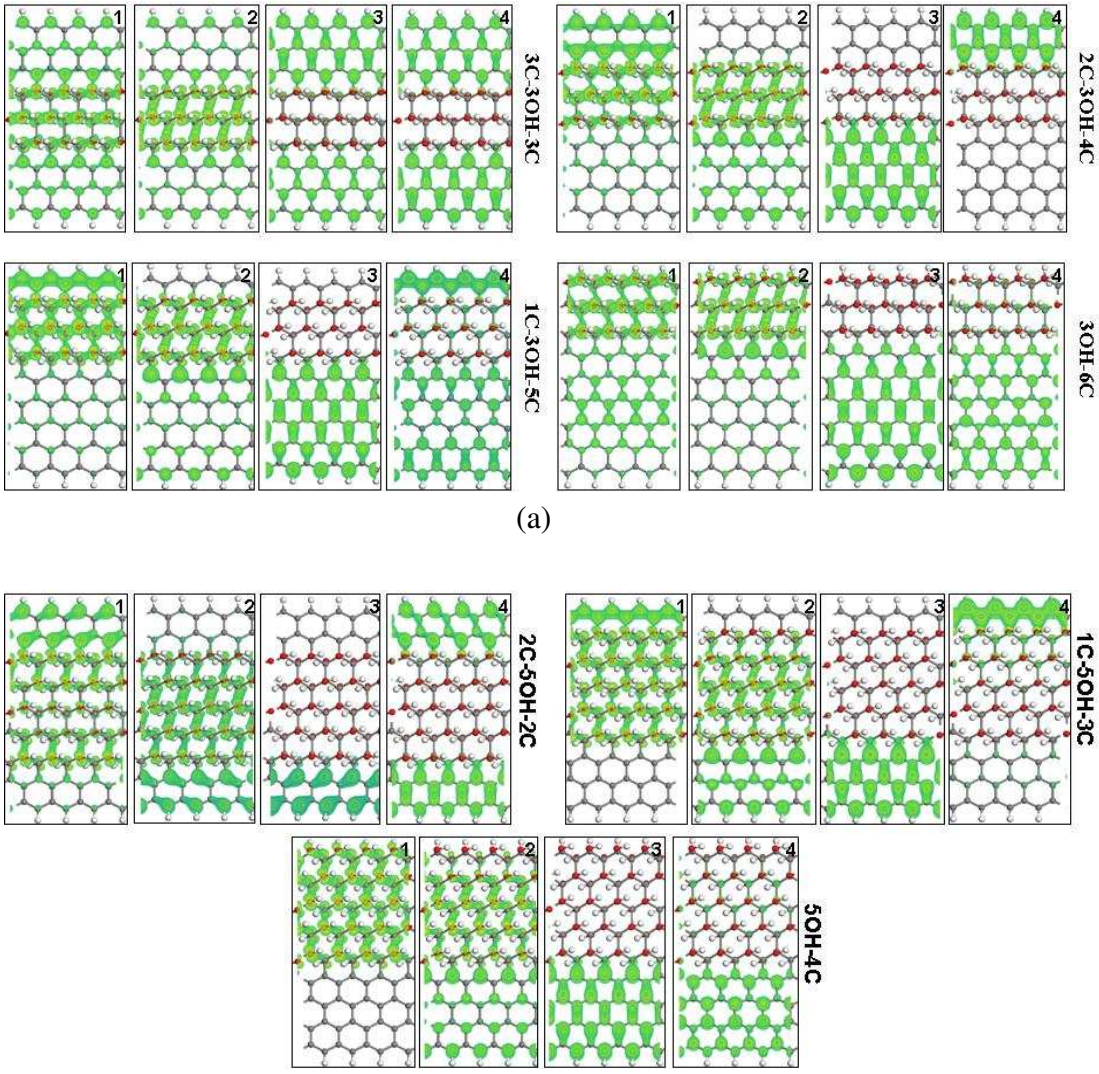


Figure S3: Band decomposed charge density distribution of (a) 9ZGNR-3OH and (b) 9ZGNR-5OH with different OH decorated positon. The numbers in the panels denote the SHVB, VBM, CBM and SLCB, respectively.

In summary, the transmission conductance around the Fermi level of 9ZGNR-3OH and 9ZGNR-5OH is sensitive to the OH decorated position. The 6 G_0 transmission plateau of 9ZGNR-3OH is depressed gradually with the movement of decoration position from the center to the edge. However, the transport properties of 9ZGNR-3OH are still enhanced in comparison with those of pristine 9ZGNR except for 3OH-6C (phase separated system) which exhibits similar transmission conductance to pristine graphene nanoribbons near the Fermi level. The semi-conductive 9ZGNR-5OH transforms into metal when the decorated position

deflects from the center. The transmission conductance of 1C-5OH-3C shows $2G_0$ to $3G_0$ plateaus when the energy is larger than -1.25 eV. 5OH-4C (phase separated system) also behaves as pristine graphene nanoribbons around the Fermi level. Such dependence of the transport properties of 9ZGNR-mOH on the decorated position derives from the energy shift of the SHVB, VBM, CBM and SLCB induced by the movement of the decorated position.