Research Article

Piezoelectric Phenomenon of Fullerene-Graphene Bonded Structure

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The adsorption of a C_{60} molecule on the graphene revealed the contribution of a conductor-semiconductor transition, based on a theoretical calculation. A stress or a strain was predicted as a possible reason to tune the transition backwards.

1. Introduction

Graphene has attracted more attention since Andre Geim and Konstantin Novoselov were rewarded the Nobel Prize in 2010 [1]. Such an advanced material was reported to be a conductor as the sp^2 hybridization of carbon atom results in a panel of networks. The electrons could move within the plane almost freely, so that the electron mobility of graphene could be up to 10^5 cm²/V sec. Thus the high-speed transistor was one of the most important applications of graphene in reality and was even predicted as the replacement of silicon in integrated circuit in the near future [2–4]. Graphane was a hydrogenated graphene as the dangling bonds of carbon atoms were all saturated by hydrogen atoms. Thus the sp^3 -like hybridization was realized and the optimized structure was revealed to be a semiconductor. Moreover, the adsorption/saturation of graphene was predicted as an important method to modify the electronic property of graphene effectively. For example, Zhou et al. obtained a band gap in graphane [5] and Surya et al. reported a band gap in the partially hydrogenated graphene [6]. All of their results indicated that graphene as well as graphane is worth studying carefully before it is used to build the nanodevices or nanocircuits.

Fullerene is another important carbon-based material as it has been synthesized and studied for decades [7–11]. Among them C_{60} was a frequent topic. Some metal atoms, ions, and clusters in or adsorbed on the C_{60} were calculated. The sp^3 - sp^2 hybridization of the carbon atom in fullerene was believed to be the reason of the special structure and activities of the quasi-0D material.

When a fullerene was close to or even bonded with a graphene, a button-like structure would be obtained. Based on this configuration, the density of states (DOS) has been studied in this work. Our results showed it a semiconductor. That is, the effect of the adsorption of the C_{60} molecule on the graphene was similar to the effect of other atoms such as hydrogen. The sp^2 hybridization was destroyed locally so that the sp^2 - sp^3 hybridization led to a band gap in the system. Moreover, when a stress or a strain was applied along the fullerene-graphene direction, the band structure would be modified accordingly. A conductor would be obtained when the strain was equal or larger than 20%. Such a finding suggested a potential nanobutton or a force/pressure sensor based on the fullerene-graphene bonded structure (FGBS), and the ON/OFF state could be controlled by a stress or a strain externally.

2. Materials and Methods

First principle calculation was employed in this work, and the configurations were all relaxed before the calculation of physical properties. Generalized gradient approximation parameterized by Perdew Burk Ernzerhof [12] was included and the norm-conserving pseudopotential [13] was used to describe the core electrons. Double zeta basis was selected to simulate the valence electrons and the cutoff of plane waves was 40 Ry.

This scheme of calculation had been tested on graphene and graphane. The former was shown as a semimetal and the latter was shown as a semiconductor. C–C bond length

FIGURE 1: Atomic structure of C_{60} -graphene bonded structure, as the bond length was indicated near the bonds. The graphene sheet was shown as an inset.

in both of them was 1.46 Å. These results were consistent with the references [14, 15] and ensured the method's validity in computing the graphene-related materials. The fullerene molecule was calculated with this method, also. The optimized structures were used to build a composite configuration.

3. Results and Discussions

Fullerene C_{60} was arranged near a graphene to a distance of 1.40 Å at first. Then the atomic positions were adjusted according to the interaction between atoms. The full-relaxed structure was shown in Figure 1. As labeled in the figure, the bond length around the fullerene-graphene connection increased to 1.56 Å or so, both in the fullerene and in the graphene. It was much larger than the C-C bond length in a graphene (~1.46 Å, shown as an inset in Figure 1). Thus a distortion was remarkable in the configuration so that the graphene sheet was not uniform any more. This was because the interaction between the fullerene and the graphene destroyed the π -bond formed in the graphene sheet locally.

The electronic properties such as the density of states (DOS) of the bonded structure were calculated and compared with those of the graphene in Figure 2. The Fermi energy level was used as the energy reference and the Gaussian broadening was 0.20 eV. It was clear that the adsorption of C_{60} led to an energy gap in the carbon-based material. Such a result was similar with the results in some other references; that is, adsorbed graphene was characterized as a semiconductor [14]. The energy gap could be attributed to the sp^3 -like hybridization that happened to the carbon atoms connecting C_{60} molecule and the graphene. Distortion due to the rebinding destroyed the sp^2 hybridization of the graphene locally as the bond length increased to a typical value in sp^3 hybridization (C-C bond length in diamond is 1.54 Å in [16]).

Next we studied the modification of the electronic properties of the FGBS. When the button-like structure was pressed along the fullerene-graphene direction, the DOS was

FIGURE 2: DOS of a C_{60} -graphene bonded structure (red line) and the DOS of a graphene (black line), with the Gaussian broadening of 0.20 eV. The differentiation of the DOS of the C_{60} -graphene bonded structure was shown as an inset and the gap width was indicated as well. The Fermi energy level was used as the energy reference.

calculated accordingly. As indicated in Figure 3, a piezoelectric phenomenon was shown clearly. When the strain was less than 20% (the estimated stress was 0.057 eV/Å³), an energy gap between the top of the valence band and the bottom of the conduction band was exhibited, where the gap width was 1.2 eV or so. (As the DOS was differentiated, the energy difference between the peaks just above and under the Fermi energy levels was 1.2 eV.) This value was close to the HOMO- (highest occupied molecular orbit-) LUMO (lowest unoccupied molecular orbit) gap of C_{60} [17]. Moreover, from the projected density of states, it was found that the carbon atoms around the graphene-fullerene connection contributed to the gap mainly. Then a script was used to control the strain

FIGURE 3: DOS of C_{60} -graphene bonded structure with the strains applied along the fullerene-graphene direction. The value of the strain was labeled and the different colors showed the DOS under different strains, namely, black for no strain, red for the strain of 7%, green for the strain of 13%, blue for the strain of 20%, light blue for the strain of 27%, and purple for the strain of 33%. The local density of states (LDOS) according to the strains of 7%, 13%, and 20% were shown as an inset to show the transition between the semiconductor and the conductor.

applied along the fullerene-graphene bonding direction. The increasing strain step was 7% and the structure was relaxed under the different strains. When the strains were, namely, 7%, 14%, 20%, 27%, and 33%, the DOS was calculated accordingly. It was interesting that as the strain increased to 20%, the energy gap disappeared thoroughly and the metallic property was shown in the DOS curve. When the strain was less than 20%, the energy gap did not vary obviously. But when the strain increased to 20%, a sudden change took place. In other cases with the strain larger than 20%, no energy gap was shown again. The gap width could be described with the formula $w = w_0 [1 - \theta(x - 20\%)]$, where the function $\theta(x)$ was a unit-step function. w showed the gap width and w_0 showed the gap value without strain. x stood for the strain applied.

It was worth noting that the electronic property of the material was modified through the applied stress or strain effectively. The electronic DOS was tightly related to the external force field. When the adsorbates were bonded with the graphene, the metallic-semiconductor transition had been revealed in some systems. But due to the fact that adsorption was usually not reversible, the metallic-semiconductor transition was not reversible either. Thus, the real application of the saturated graphene was limited. The C_{60} -graphene bonded structure was different, as the bonded structure showed metallic or semiconductor character in the same system. The atomic structure need not be destroyed, and the metallic-semiconductor transition only relied on the stress or the strain applied externally. It means that the FGBS was desired to be used as a button in nanometer scale. If the metallic state is labeled as ON while the semiconductor state is labeled as OFF, the ON/OFF switch could be controlled through changing the stress or strain directly.

Such a finding also suggested the FGBS, a force/pressure sensor in nanoscale. When the force or pressure applied on it was large enough, there should be some electric signal output based on a necessary external circuit. As the synthesis of fullerene and the graphene was mature and the bonding between them could be realized in experiments [18], such a sensor should be synthesized and applied in the near future.

In the further study of the C_{60} -graphene bonded structure, it was found that the bonds were the main reasons of the piezoelectric effect. When the stress was larger than $0.02 \text{ eV}/\text{\AA}^3$, the local structure around the connection was much closer to that in the graphene without adsorption. The sp^2 -like hybridization was related to the π -bond as well as the electron transport. Thus the energy gap vanished and the metallic property was revealed.

As follows the local density of states (LDOS) was calculated and shown as an inset in Figure 3. It was interesting that the influence of the strain could be found extending gradually. When the strain was 7%, the maximum of the LDOS could be found around the graphene-fullerene connection. But as the strain increased, the change of LDOS took place in a large area. The LDOS near the fullerene decreased and the LDOS far away from the fullerene increased obviously. The conductor character was revealed just when the strain was released on the whole graphene panel.

It was noted that the strain making the semiconductor-metallic transition was large so that the sensitivity was not satisfying. But it was believed that the molecule adsorption was a new method to decorate the graphene, and some other adsorbates or adsorption details should improve the sensitivity definitely.

4. Conclusions

In this work, the C_{60} -graphene bonded structure was studied with numerical calculation. The chemical bonds connecting them were found close to those in diamond, so that the energy gap was shown. But when the strain along the C_{60} -graphene direction was applied, a semiconductor-conductor transition could be realized. Our results evidenced that the molecule adsorption on graphene could be used as a nanobutton or force/pressure sensor, due to the interesting piezoelectric phenomenon.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

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