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Breaking surface states causes transformation from metallic to semi-conducting behavior in carbon foam nanowires

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ABSTRACT

Carbon foam nanowires (CFNWs), which are mixed sp^2/sp^3 hybridized microporous one-dimensional structures, have received much attention in the past two decades. In the present work, first-principle and molecular dynamics (MD) calculations revealed that the surface states causes the metallicity of CFNWs with small size, which demonstrates a Dirac cone-like dispersion near Γ in the Brillouin zone, while the metallicity of large size CFNWs are caused by the bulk states. However, hydrogenation of the CFNWs turns the metallicity into semiconducting with an expansion of the band gap by 0.15–1.5 eV. Interestingly, the metallicity is enhanced when hydrogenation on the top of the CFNWs. Atomic cohesive energy analysis suggests that the CFNWs are energetically favorable up to its melting point at 2200 K. When heating above the melting point, CFNWs transit into multi-walled carbon nanotubes (MWCNTs), agreeing with experimental observations. These findings indicate the feasibility of metallic-semiconductive transition, which have potential applications in nanoscale devices, hydrogen storage and the preparation of MWCNTs.

1. Introduction

One-dimensional (1D) metallic or semiconductor nanowires have been proposed as important components of future integrated circuits as they are integral to the design and construction of electronic and optoelectronic devices [1] as well as thermoelectric devices [2–4]. Nanowires formed by carbon materials possess huge application prospects owing to their fascinating mechanical and electronic properties. It is well known that the diversity of carbon-based materials mainly arises from the three hybridizations of carbon atoms, that is, *sp*, sp^2 and sp^3. Examples of carbon-based nanowires are carbyne [5], carbon nanotubes (CNTs) [6] and diamond nanowire [7], which are *sp*, sp^2 and sp^3 hybridized nanowires, respectively. However, there are mixed hybridization carbon-based nanowires besides the pure hybridization types; as examples, a multi-walled carbon nanotube (MWCNT)-carbyne carbon nanowire contains both *sp* and sp^2 hybridized atoms [8], and amorphous carbon nanowires have a mixed sp^2/sp^3 bonding character [9–14]. Among them, amorphous carbon nanowires may show more attractive electronic and optical properties owing to their microporosity.

In fact, amorphous carbon nanowires are part of carbon foam (CF) materials [15–20], which are formed by sp^2 graphene strips interconnected by sp^3 C atom junctions. The infinite extension of these junctions throughout the real space results in a periodic porous three-dimensional (3D) network, which resembles the structure of a foam. The amorphous carbon nanowire is thus called a carbon foam nanowire in this work. Depending on the two types of the graphene edge shapes—that is, zigzag and armchair—and the number of hexagonal units between sp^3 junctions, Agnieszka et al. [21] defined different types of CF as *Zig(N,M)/Arm(N,M)*, where *(N,M)* signifies the pore size of the CF. The rich and unique properties provide CF with huge potential for application. For example, taking advantage of porosity, researchers have used CF for hydrogen storage [22–25], energy storage [26] and molecular sieving [15]; the light weight and high surface area make CF a non-negligible candidate for the manufacture of supercapacitors [27,28]; and the metallic oxide nanoparticles encapsulated within the hole of 3D CF can be used as the electrode for a lithium ion battery [29–31]. Moreover, the conductivity of CF at room temperature could reach 1.3×10^5 S/m [32] and the thermal conductance spans over a wide range [33–35], which indicate its potential

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application in thermoelectric devices. Carbon foam nanowires (CFNWs) inherit the advantages of the CF material. Besides, CFNWs show a wide electrochemical stability window, outstanding biocompatibility, high thermal conductivity, and high surface-to-volume ratio [9]. Meanwhile, the mixed sp^2/sp^3 bonding makes the electronic and optical properties of CFNWs different from those of CNTs.

In the past, CFNWs were mainly obtained by thermal evaporation and ion bombardment. The former method was first proposed by Tang et al. [11], who annealed a pressed tablet of graphite powder mixed with nickel at 1200 °C and collected the soot containing the amorphous CFNWs from the inner wall of a quartz tube. Their further studies, using HRTEM and NEXAFS, presented evidence that amorphous CFNWs are precursors to the formation of multiwall carbon nanotubes and can be converted to a MWCNT upon annealing [12]. The latter method was performed by Ni et al., who applied a 40-KeV Si ion beam to irradiate a template of MWCNTs, which were then transformed into CFNWs [10]. To date, many methods have been applied to synthesize and use CFNWs. Han et al. [14] used Fe/Al_2O_3 catalytic CVD processes to obtain both SWCNT and CFNWs networks by slightly altering the hydrogenation and temperature conditions. By applying standard lithography, oxygen plasma treatment and thermal processing, Michaël et al. [9] synthesized and integrated amorphous CFNW forests, which were perpendicular to the substrate. The high surface area meant the networks could be chemically functionalized and used for measurement of DNA binding with increased sensitivity. Qiu et al. [13] used a facile morphology-conserved approach in tandem with subsequent calcination in a mixture of hydrogen and argon to synthesize a composite where hyperfine *Sn* nanoparticles were encapsulated in the holes of the CFNWs, and the composite was used as the anode of rechargeable lithium ion batteries.

Even though significant works on CFNWs have been performed experimentally, these studies have mainly focused on synthesis and applications, with a few focusing on the structures, stabilities and electronic properties. A theoretical study, to the best of our knowledge, is yet to be performed as a follow-up on the experimental research. Here, we perform first-principle calculations combined with molecular dynamics calculations to simulate the electronic properties accompanying the accommodation and stabilities of a zigzag (1,1) carbon foam nanowires. In the first part of this work, the structures of CFNWs are illustrated. It is interesting to observe that CFNWs are energetically more favorable than its bulk from the cohesive energies analysis. Next, we calculate the electronic structures of CFNW with different sizes. The results indicate that the surface states, which play a critical role in the behavior of electrons near the Fermi levels, form a Dirac cone-like dispersion near Γ in small-diameter CFNWs. Then, we tried to passivate the surface states by hydrogenation technology in the third part. It is interesting to find that the electronic properties that change from metallic to semi-conductive are induced by different hydrogen coverage rates and hydrogenated positions, with band gaps ranging from 0 to 1.5 eV. Finally, the thermal stability studies of the CFNW suggest that the CFNW is quite stable at room temperature and remains stable until 2200 K, which is comparable to its bulk at 2300 K, and the CFNWs tend to melt into multi-walled carbon nanotubes when the temperature is further increased, which accords well with the experimental observation [12].

2. Calculation methods

The electronic structure calculations are carried out with density functional theory (DFT), as implemented in the Vienna ab-initio simulation package (VASP) [36,37]. Within the frame of DFT, the electron–ion interaction is described by the projector augmented-wave (PAW) potential, and the generalized gradient approximation (GGA) is adopted to describe the interaction between electrons. The kinetic energy cutoff for the plane wave basis set was 520 eV. The $1 \times 1 \times 9$ Γ centered Monkhorst-Pack grids were generated to mesh the reciprocal space of all nanowire structures. The energy convergence criteria for electronic self-consistent iterations were set to be 10^{-4} eV, and the structure relaxation proceeded until the force on each atom was less than 0.01 eV/Å. The energy-dependent conductance was calculated with DFT combining non-equilibrium Green's functions, which was implemented in the Atomistix ToolKit (ATK) package [38,39].

The thermal stability was studied by performing molecular dynamics (MD) simulations, which were implemented in the LAMMPS package [40]. With increasing temperatures, a Nose-Hoover thermostat [41,42] was adopted to keep the systems in equilibrium for at least 2.5 ns at a given temperature. To avoid the artifacts caused by small unit cells in our simulations, we created a supercell of CF that contained 1080 atoms and supercells of CFNWs with lengths of 4.26 nm. The time step was set as 0.5 fs, and the Tersoff potential [43] was used to simulate the interaction between atoms.

3. Results and discussion

3.1. Structures and chemical stability

Inspired by the recent works on amorphous carbon nanowires [9–14], the hypothetical zigzag (1,1) CFNWs were constructed, as illustrated in Fig. 1. Fig. 1(a) depicts the structure of the zigzag (1,1) CF bulk, in which sp^2 and sp^3 hybridized C atoms bond orderly to form a porous 3D network. The optimized hexagonal lattice, denoted by black lines in Fig. 1(a) where a = b = 4.841 Å and c = 4.173 Å, is comparable to that formerly reported in Ref. [19]. Fig. 1(b) depicts the cross-sectional view of CFNW. As one can see, the distinct colors change with the diameter of the nanowires. We denoted the different sizes of an intact CFNW by the numbers of hexagonal hole in its cross-section. The minimum diameter of the zigzag (1,1) CFNWs is a (6,0) CNT with only one hole in the cross-section (as shown in orange in Fig. 1(b)), denoted as 1H-CFNW. As the diameter increases, the cross-section of CFNWs consists of 7 holes, 19 holes, 37 holes, and so forth, resembling bundles of (6,0) CNTs, which were denoted as 7H-CFNW, 9H-CFNW, 37H-CFNW, and so forth, respectively. The numbers of surface *sp2* C atom, inside *sp2* C atom and *sp3* C atom of 7H-, 19H- and 37H-CFNW are (60, 24, 24), (96, 84, 72) and (132, 180, 144), respectively. The lattice constant of the CFNW unit cell in Fig. 1(c) is c = 4.26 Å, which is slightly larger than that of the bulk owing to the structural reconstruction caused by the existence of surfaces. In the unit cell of CFNWs, the vacuum space of 20 Å in every direction of non-periodicity was included to avoid the interaction between CFNWs.

The structure reconstruction will change the bond lengths and bond angles of the nanowires when compared with the CF bulk, and some sp^3 hybridized C atoms on surface are changed into sp^2 hybridized atoms. To inspect the chemical stability of the CFNWs, we calculate the structure parameters and average cohesive energy (E_{coh}) of CFNWs as well as several carbon-based materials, as shown in Table 1. The cohesive energy per C atom is calculated by the formula [44]:

$$E_{coh} = -\left(\frac{E_{Total}}{N_C} - \mu_C\right), \quad (1)$$

where E_{Total} is the total energy of the carbon based material unit, N_C and μ_C is the total number and chemical potential of C atoms, respectively.