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Structural and electronic properties of copper nanowires inside zigzag carbon nanotubes

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ABSTRACT

We present a systematic study of the structural and electronic properties of Cu_N@(n,0) (N=1, 2, 4 for n=6, 7, 8 and N=12, 16 for n=10) combined systems using the first-principle calculations. We find that CuNWs encapsulated inside the (6,0) CNTs prefer to form a single linear chain on the tube axis, while those in (7,0) and (8,0) CNTs tend to form a zigzag chain. The smaller formation energies of −2.265 eV for Cu_{12}@(10,0) combined system and −2.271 eV for Cu_{16}@(10,0) combined system indicate that these two systems are more stable than the other systems studied here, and more complex configurations of CuNWs are expected encapsulating into broader CNTs. Besides having high stability, the Cu_{16}@(10,0) combined system with quantum conductance of $3G_0$ is under the protection of the outer (10,0) CNT from oxidation, thus can be expected to have potential applications in building nanodevices. The asymmetry distribution of the down-spin and up-spin channels results in a net magnetic moment of 0.59μB for the Cu_2@(7,0) combined system.

1. Introduction

Carbon nanotubes (CNTs) have attracted considerable attention, owing to their special properties and intriguing applications in many fields [1–3]. CNTs filled or adsorbed with metals can combine the electronic and magnetic properties of the metals with the electrical property of the CNTs, and show potential applications in diverse fields, for example in microwave absorption [4], magnetic storage [5], human tumor therapy [6] and probe of the magnetic force microscopy (MFM) [7]. To date, several methods of encapsulating or adsorbing metals to CNTs have been developed, such as the wet chemical method [4], powder pyrolysis method [7–9], arc-discharge technique [10], templated-assisted method [11], and so on.

Since copper is a typical conductive metal with very high thermal and electrical conductivity, Cu atoms filled in or adsorbed on CNTs have been therefore the subjects of many theoretical [12–15] and experimental [16–20] studies. The introduction of metals into CNTs may significantly alter their conducting, electronic, magnetic and mechanical properties, as well as altering the properties of metals. Durgun et al. systematically studied the adsorption of individual transition atom on the perfect (8,0) and (6,0) CNTs. They found that the interaction between the nonmagnetic Cu atoms and nonmagnetic (8,0) CNT results in a magnetic ground state for the combined system with a net magnetic moment 0.53μB [14]. Du et al. made a first-principle study on the Cu_8 nanowire encapsulated semiconductor zigzag CNTs, showing that the strong metallic character of Cu_8 nanowire gives the combined system a metallic character [15]. In the CNTs covering metal core combined systems, the carbon shells provide an effective barrier against oxidation and ensure long-term stability of metal core [21,22]. Since CNTs have excellent mechanical properties and diverse electronic structures that can be either metallic or semiconducting depending on the chirality and diameter [23], the electronic state hybridization between CNTs and the size-confined ultrathin copper nanowires (CuNWs) may open a way of tailoring the electronic structures of CNT-based material. Hence, the CNTs covering CuNWs have a significant potential application in ultra-large-scale integration (ULSI) circuit and micro-electromechanical systems (MEMS) of the future. Moreover, the dimerization effects that dominate the electronic properties of one dimensional metal atomic chain may also play an important role in tube-wire combined system. However, the knowledge of these aspects is still missing.

In the present work, the structural and electronic properties of CuNWs with different Cu contents encapsulated inside zigzag (n,0) CNTs (n=6, 7, 8 and 10) have been investigated in detail by using the first-principle projector-augmented wave (PAW) potential

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within the density-functional theory (DFT) framework under the generalized-gradient approximation (GGA). For simplicity, these combined systems are denoted by $Cu_N@(n,0)$ ($N=1, 2, 4$ for $n=6$, 7, 8 and $N=12$, 16 for $n=10$) throughout the paper, where the subscript N of Cu indicates the number of Cu atoms per supercell. The rest of the paper is organized as follows. In Section 2, the calculation methods are given. In Section 3, the optimized structures of $Cu_N@(n,0)$ combined systems ($N=1$, 2, 4 for $n=6$, 7, 8 and $N=12$, 16 for $n=10$) are presented. The dependence of electronic structure on the diameter of the CNTs and on the atomic arrangement in the encapsulated CuNWs is also discussed. Finally, the conclusions of the work are presented in Section 4.

2. Calculation methods

All calculations are performed by using Vienna ab initio simulation package (VASP) [24–26] based on the density-functional theory (DFT), with the PAW potentials and plane waves basis set [27]. The $2s^2 2p^2$ and $3d^{10} 4s^1$ electrons are taken as the valence electrons for C and Cu atoms, respectively. To treat electron exchange and correlation, we choose the Perdew–Burke–Ernzerhof [28] formulation of the GGA, which yields the correct ground-state structure of the combined system. All structures have been treated within supercell geometry using the periodic boundary conditions. We choose two unit cells of the CNTs as a supercell for encapsulating CuNWs. In order to provide a large vacuum space more than 16 Å, the lattice constants a and b of the tetragonal supercell in the plane perpendicular to the tube axis range from ~20.54 to ~23.73 Å, depending on the diameter of the CNTs, and that along the tube axis is taken as $c=2c_0$, where c_0 (4.26 Å) is the lattice constant of the CNT along tube axis. The wave functions are expanded in a plane-wave basis set with an energy cutoff of 400 eV. The Brillouin zone integration is performed within the Gamma centered Monkhorst-Pack scheme [29] using $(1\times1\times15)$ k-points. All the quasi one dimensional geometric structures are fully relaxed to minimize the total energy of the system until a precision of 10^{-4} eV/atom is reached. The conjugate gradient minimization is used for optimization of the atom coordinates until the force acting on each atom is smaller than 0.02 eV/Å.

In order to test the quality of the above parameters, the lattice parameter and binding energy for bulk Cu crystal in the face centered cubic (FCC) lattice have been calculated. The calculated lattice constant and binding energy of bulk Cu are 3.626 Å and 3.47 eV, respectively, which are in good agreement with corresponding experimental values of 3.615 Å and 3.49 eV [30]. The calculated lattice constant also agrees well with previous DFT–GGA value 3.64 Å [31].

3. Results and discussions

3.1. Structural properties

The optimized structures of $Cu_N@(n,0)$ ($N=1$, 2, 4 for $n=6$, 7, 8 and $N=12$, 16 for $n=10$) combined systems are plotted in Fig. 1 from both the top views and side views. The optimized diameters of the CNTs, distances between two neighbor Cu atoms (d_{Cu-Cu}) and the angles (α) of the Cu–Cu bond deviation from the tube axis are listed in Table 1 together with the diameters of the corresponding pristine CNTs for comparison.

We first consider the Cu filled (6,0), (7,0) and (8,0) combined systems containing a single Cu atom per supercell; the corresponding optimized structures are plotted in Fig. 1(a), (d) and (g). The Cu atoms in these tubes align linearly on the tube axis and form a single chain with equal Cu–Cu distance of 8.520 Å. It is interesting to note that the different stable sites are obtained for a single Cu chain in these tubes. For the $Cu_1@(6,0)$ combined system, Cu atom is located at the center of a zigzag ring, whereas for $Cu_1@(7,0)$ and $Cu_1@(8,0)$ combined systems, Cu atom is located at the center of two neighbor zigzag rings. This indicates that the relative position of a single Cu chain with respect to the outside thin CNTs is curvature dependent, which is different from the case of a single metal atom adsorbed on the exterior wall of the CNTs, where the adsorbed atom is always located right above the center of a carbon hexagon [32].

The relative stabilities of the $Cu_N@(n,0)$ combined systems can be estimated by the formation energy E_{form}

$$E_{form} = (E_{Cu_N@(n,0)} - E_{(n,0)} - NE_{Cu})/N$$

where $E_{Cu_N@(n,0)}$, $E_{(n,0)}$ and E_{Cu} are the total energies of the $Cu_N@(n,0)$ combined system, corresponding pristine $(n,0)$ CNT and isolated Cu atom, respectively, and N is the number of Cu atoms per supercell. The calculated formation energies are summarized in Table 1 for more quantitative comparisons. The negative (positive) formation energy indicates that the formation process is exothermic (endothermic). Variations of the formation energy E_{form} for a single Cu chain moving inside $(n,0)$ CNTs ($n=6$, 7 and 8) along the path A→B→A on the tube axis are plotted in Fig. 2(a). The red points A and B on the (6,0) tube axis in inset plot show the stable sites of the Cu atom. We can see that the formation energies of $Cu_1@(6,0)$ and $Cu_1@(7,0)$ combined systems are always negative for Cu atom located at different sites on the tube axis, indicating that the stable structures corresponding to a local minimum on the Born–Oppenheimer surface [33] and the formation processes are exothermic. While for the $Cu_1@(8,0)$ combined system, the positive formation energies are obtained for Cu atom located at different sites on tube axis, indicating that the formation processes are endothermic. In addition, the formation energies have a local minimum at site B for the $Cu_1@(6,0)$ combined system, whereas for both $Cu_1@(7,0)$ and $Cu_1@(8,0)$ combined systems the local minimum appears at site A. Variations of the formation energy for a single Cu chain moving inside $(n,0)$ CNTs ($n=6$, 7 and 8) along the radial direction are plotted in Fig. 2(b). The vertical dashed lines indicate the positions of the respective nanotube walls. The inset shows the nanotube radius R and the axial separation r of a single Cu chain from the tube axis. The formation energies of $Cu_1@(6,0)$ and $Cu_1@(7,0)$ combined systems are negative in the range of axial separation $r<0.43$ Å and $r<0.69$ Å, respectively. The curve slope of the combined system with smaller tube diameter is larger than that of the combined system with larger tube diameter. Furthermore, from wider region near the formation energy minimum of the $Cu_1@(7,0)$ and $Cu_1@(8,0)$ combined systems we can speculate that a single Cu chain encapsulated inside larger nanotube would still have some degree of lateral freedom and even more than one Cu chain can be encapsulated into the larger nanotube by forces amounting to a fraction of a nano-Newton. The larger the CNT's diameter, the wider the space provided for the Cu chain to move along the radial direction. Hence, for the nanotube with larger diameter, it can accommodate the CuNW with larger diameter.

The optimized structures of $Cu_2@(6,0)$, $Cu_2@(7,0)$ and $Cu_2@(8,0)$ combined systems are plotted in Fig. 1(b), (e) and (h), respectively. For the $Cu_2@(6,0)$ combined system, Cu atoms locate on the tube axis and form a linear chain with equal Cu–Cu distance of 4.26 Å (half the length of the supercell along tube axis). The side view of the supercell shows that the Cu atoms locate at the center of interval zigzag rings (site B). For the $Cu_2@(7,0)$ combined system, the encapsulated Cu atoms still align linearly on the tube axis and form a linear chain, but the Cu–Cu distances are no longer equal (2.360 Å and 6.160 Å alternatively). Similar dimerization character