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Energetics and electronic structure of a single copper atomic chain wrapped in a carbon nanotube: a first-principles study*

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In the generalized gradient approximation, the energy and electronic structure are investigated for a single copper atomic chain wrapped in (4, 4), (5, 5) and (6, 6) armchair carbon nanotubes by using the first-principles projector-augmented wave potential within the framework of density functional theory. The results show that the (4, 4) and (5, 5) tubes are too narrow to wrap a Cu chain, but the (6, 6) tube is nearly ideal to wrap a Cu chain on its centre axis. Wider tubes are anticipated to wrap more than one Cu chain spontaneously with forces amounting to a fraction of a nanonewton. Although the tube–chain interaction decreases with the increase of the tube diameter of (4, 4), (5, 5) and (6, 6) successively, the charge density of the Cu@(6, 6) combined system still does not show complete superposition of that of the pristine (6, 6) tube and Cu chain. Successively reducing the restrictions of (4, 4), (5, 5) and (6, 6) tubes on the Cu chain leads to a reduction in shift of the highest peak of the Cu chain towards lower energies, that is from −0.5177 eV of the isolated Cu chain to −1.36785 eV, −0.668 eV and −0.588 eV for the Cu@(4, 4), Cu@(5, 5) and Cu@(6, 6) systems, respectively. In reverse, the strong metallic character of the Cu chain also enhances the metallic character of the combined systems so that the broader pseudogaps of the pristine carbon nanotubes around the Fermi level change into the narrow pseudogaps of the combined systems.

Keywords: copper atomic chain, carbon nanotube, electronic structures, first-principle
PACC: 7320D, 7125X, 2110D, 7115A

1. Introduction

Carbon nanotubes (CNTs) have attracted much attention, owing to their special properties and intriguing applications in many fields.[1−14] It has been demonstrated that they possess remarkable mechanical properties and interesting electric transport behaviours and thus can be used in nanoelectronic devices, energy storage, field emission displays, chemical and biological sensors, and other technological aspects.[15,16] Due to their hollow cylindrical structures,[17] the CNTs could serve as containers for atoms and small molecules.[18−21] In this regard, they could be also used for hydrogen storage.[22] In particular, CNTs filled with metals represent a fascinating new material and are an effective route to exploit one-dimensional nanocables in various usages. These CNTs covering metal chains or nanowires have a significant potential application in data storage nanotechnology due to their small size. In addition, the carbon shells provide an effective barrier against oxidation and consequently ensure the long-term stability of the metal core.[23−27] Recently, CNTs filled with copper have been fabricated successfully in experiments,[28,29] but few studies on energetics and electronic structures of copper atomic chain wrapped in CNTs have been reported in detail. As a piece of fundamental research, in the present work the binding energies and the electronic structures of a single copper atomic chain encapsulated in (4, 4), (5, 5) and (6, 6) armchair CNTs are investigated in detail. The calculation is also performed on an isolated Cu atomic chain and pristine nanotubes for comparison.

The remainder of the present paper is organized as follows. In Section 2, the calculation method and the model of a single Cu atomic chain wrapped in CNTs are given. In Section 3, the binding energies and electronic structures of copper atomic chain wrapped in CNTs are analysed. Finally, the conclusions of the work are drawn in Section 4.

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2. Calculation method and model

The calculations in this paper are performed within the framework of the density functional theory (DFT) by using the projector-augmented wave (PAW) potentials[30] and a plane-wave basis set as implemented in the Vienna *ab-initio* Simulation Package (VASP) computer code.[31−34] Normally, the PAW potentials are more accurate than the ultrasoft pseudopotentials and require a higher cutoff energy. We thus use a uniform 500 eV for all the calculations, which is much higher than 273 eV and 400 eV for Cu and C, respectively, specified in their PAW potentials. The $3d^{10}4s^1$ and $2s^22p^2$ electrons are taken as the valence electrons for Cu and C atoms, respectively. The electron exchange and the electron correlation are treated by using the Perdew–Burke–Ernzerhof (PBE) formulation of the generalized gradient approximation (GGA).[35] We choose a conjugate-gradient algorithm to relax the ions into their ground states, and the energies and the forces on each ion are converged to less than 10^{-5} eV/atom and 0.02 eV/Å (1 Å=0.1 nm), respectively. The Brillouin zone (BZ) integration is performed within the Monkhorst–Pack scheme[36] by using 1×1×15 k points. We set the periodicity of the CNT along the CNT axis direction, and a 15-Å vacuum region perpendicular to the CNT axis direction in order to avoid interaction between CNTs.

As an example, figure 1 schematically shows a simple model for a single Cu atomic chain bound in an armchair (6, 6) CNT denoted as Cu@(6, 6) for convenience. The unit cell contains 25 atoms. Of these, a Cu atom is associated with the Cu atomic chain and located in the direction perpendicular to the tube wall through the centre of a hexagon by carbon–carbon bonds.

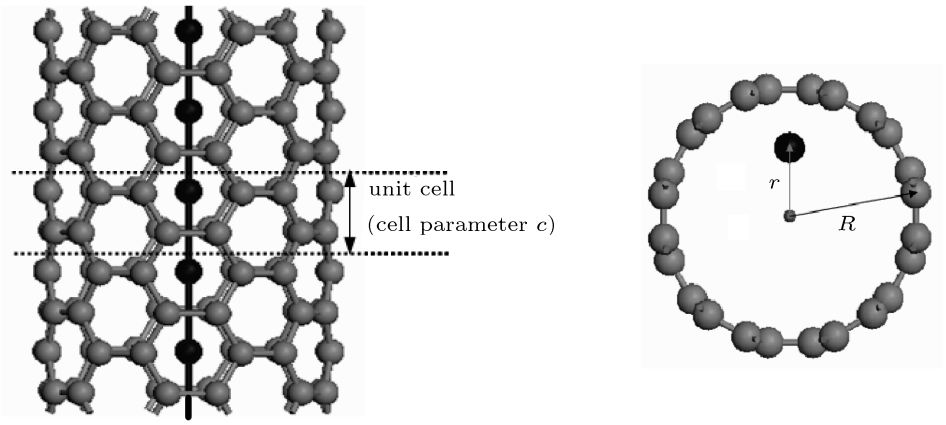


Fig.1. Side (left) and top (right) views of a periodic boundary model of a single Cu atomic chain bound in the (6, 6) C nanotube. The black and grey balls represent the Cu and C atoms respectively. The nanotube radius R and the axial separation r of the Cu atomic chain are also shown in the top view (right).

3. Results and discussion

3.1. The binding energy

The relative stabilities of Cu@(n, n) $(n = 4, 5, 6)$ combined systems can be determined by the binding energy ΔE

$$\Delta E = E_{\mathrm{Cu@}(n,n)} - (E_{\mathrm{Cu}} + E_{(n,n)}),$$

where $E_{\mathrm{Cu@}(n,n)}$, E_{Cu} and $E_{(n,n)}$ are the total energies of the Cu@(n, n) combined system, isolated Cu atomic chain, and pristine (n, n) CNTs, respectively.

Figure 2 shows the binding energy ΔE between a single Cu atomic chain and various (n, n) nanotubes as a function of the axial separation r. The energies are given per unit cell and the vertical arrows for $R(n, n)$ indicate the positions of the respective nanotube walls. The binding energies of the Cu@(4, 4) or Cu@(5, 5) systems are always positive, indicating that the interactions between the (4, 4) or (5, 5) nanotube and Cu atomic chain are always repulsive and these two CNTs are too narrow to accommodate a single chain. In other words, the insertion processes are completely endothermic for these two kinds of nanotubes. For the (6, 6) nanotube, the nanotube diameter is sufficient to allow a single Cu chain to be wrapped in the nanotube.

From energy minimization, we know that the most stable position of the Cu atomic chain is just on the centre axis of the (6, 6) nanotube. Furthermore, the wider binding energy minimum of the (6, 6) nanotube implies that a single Cu atomic chain encapsulated inside a (6, 6) nanotube would still have some degree of lateral freedom so we can speculate that even more than one Cu chain can be pulled spontaneously into the open nanotubes by forces amounting to a fraction of a nanonewton.

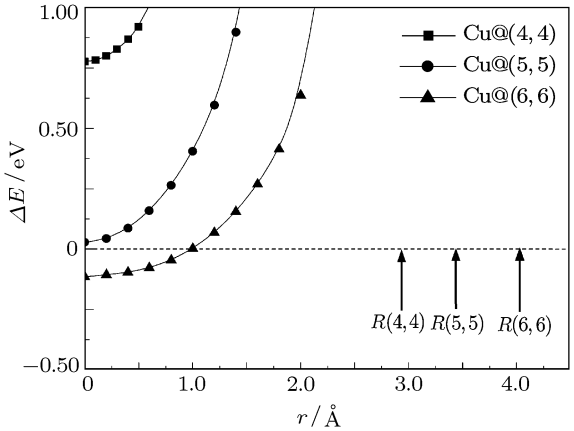


Fig.2. Values of binding energy ΔE between a single Cu chain and a (4, 4), (5, 5) or (6, 6) C nanotube as a function of the axial separation r of the Cu atomic chain, separately.

3.2. Electronic structures

Figure 3 shows the contour plots of charge density distribution in the plane perpendicular to the system axis and through the Cu atom site for an isolated (a) Cu chain, (b) (4, 4), (c) (5, 5) and (d) (6, 6) carbon nanotubes, and (e) the Cu@(4, 4), (f) Cu@(5, 5) and (g) Cu@(6, 6) combined systems. The nanotube–Cu interaction can be understood further from these contour plots. In the Cu@(4, 4) system, a very high charge density appears between the Cu chain and the carbon nanotube, indicating a strong nanotube–Cu repulsive interaction. As the diameter of the carbon nanotube increases, the nanotube–Cu interaction is weakened. But even in the Cu@(6, 6) system, the charge density does not show complete superposition of those of the pristine (6, 6) carbon nanotube and Cu chain, reflecting a very weak interaction still exists between the components of the combined system. In addition, since this charge stems predominantly from the nanotube, we can talk about Cu-induced hole doping of the nanotube, similar to double-walled carbon nanotubes.[37] We educe that virtually, because of the nonvanishing interaction, armchair carbon nanotubes do not act as 'perfectly inert' containers for a Cu chain.

Better insight into the degree of electronic interaction between the CNT and Cu chain can be gained from analyses of the band structures and density of states (DOS). Shown in Fig.4 are the band structures for an isolated Cu chain, (4, 4), (5, 5), (6, 6) CNTs and the Cu@(4, 4), Cu@(5, 5), Cu@(6, 6) combined systems. The Fermi level $E_{\rm F}$ is set to zero energy and indicated by the solid line. It can be seen that, firstly, for three pristine (4, 4), (5, 5) and (6, 6) CNTs there are bands crossing the Fermi level $E_{\rm F}$ at about three fifths of the distance between Γ and Z, implying a metallic character. This is because these three CNTs satisfy the rule that $2m + n$ is a multiple of three.[15] Secondly, the electronic band structures of the CNTs have been significantly modified by inserting a single Cu chain especially for the narrow (4, 4) CNT in which the Fermi level shifts obviously toward the conduction band of the carbon nanotube. Such a shift was also observed for an aluminium atomic chain wrapped in (4, 4) CNT.[38] As the diameter of the carbon nanotube increases, the band structures of the combined systems are analogous to the superposition of their components. Shown in Fig.5 are the densities of states for an isolated Cu chain, (4, 4), (5, 5), (6, 6) CNTs and the Cu@(4, 4), Cu@(5, 5), Cu@(6, 6) combined systems. A comparison of the DOSs of three pristine (4, 4), (5, 5) and (6, 6) CNTs shows that the effects of inserting a Cu chain on the DOS of three pristine (4, 4), (5, 5) and (6, 6) CNTs are mainly near and below the Fermi level $E_{\rm F}$ (dashed line), but the DOS of the combined systems does not show complete superposition of those of the individual nanotube and Cu chain, indicating some degree of electronic interaction between the valence systems of the two structures. The highest peaks B, C and D respectively in the Cu@(4, 4), Cu@(5, 5) and Cu@(6, 6) combined systems are obviously contributions of the highest peak A of the Cu chain, successively reducing the restrictions of (4, 4), (5, 5) and (6, 6) CNTs on the Cu chain leads these highest peaks B, C and D each to have a reduction in shift towards lower energies, that is from −0.5177 eV of the isolated Cu chain to −1.36785 eV, −0.668 eV and −0.588 eV for the Cu@(4, 4), Cu@(5, 5) and Cu@(6, 6) systems, respectively. In reverse, the strong metallic character of the Cu chain also enhances the metallic character of the combined systems as indicated by the fact that the broader pseudogaps of pristine CNTs around the Fermi level change into the narrow pseudogaps of the combined systems.

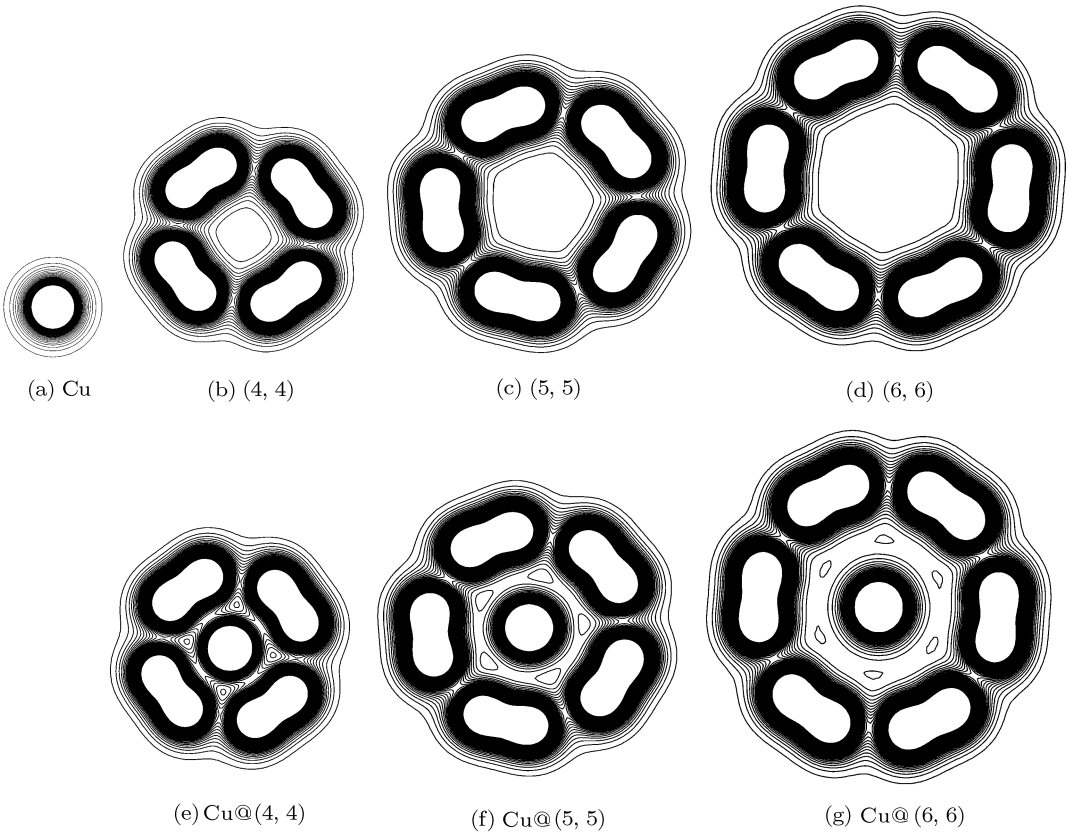


Fig.3. Contour plots of charge density distribution in the plane perpendicular to the system axis and through the Cu atom site for an isolated (a) Cu chain, (b) (4, 4), (c) (5, 5) and (d) (6, 6) carbon nanotubes, and (e) the Cu@(4, 4), (f) Cu@(5, 5) and (g) Cu@(6, 6) combined systems. All contours start from 0.014 and change successively by a factor of 0.014.

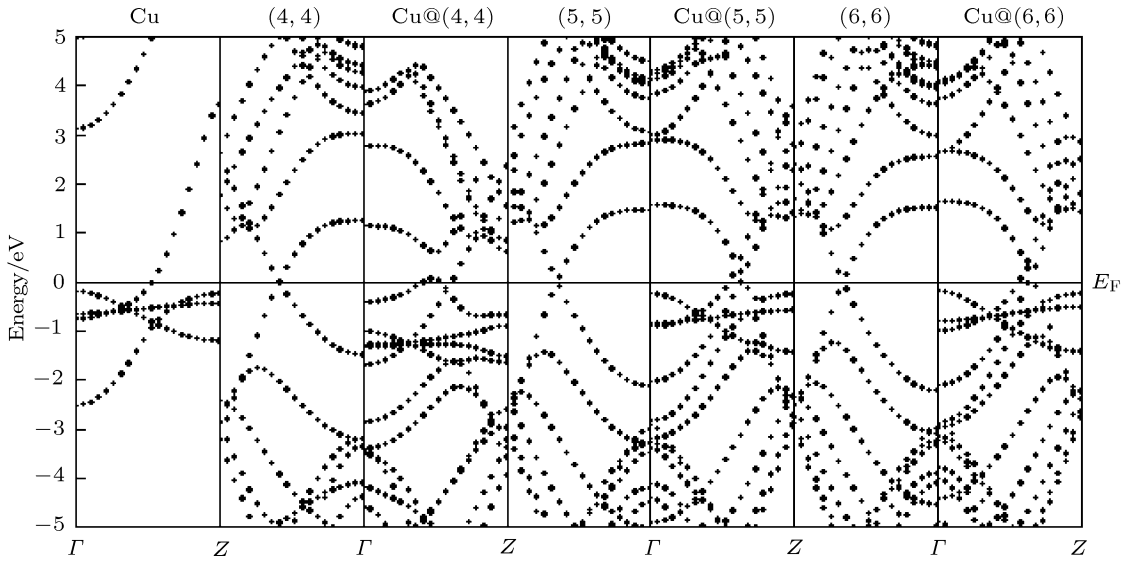


Fig.4. Band structures for an isolated Cu chain, (4, 4), (5, 5), (6, 6) carbon nanotubes and the Cu@(4, 4), Cu@(5, 5), Cu@(6, 6) combined systems. The Fermi level E_F is set to be at zero energy and is indicated by the solid line.

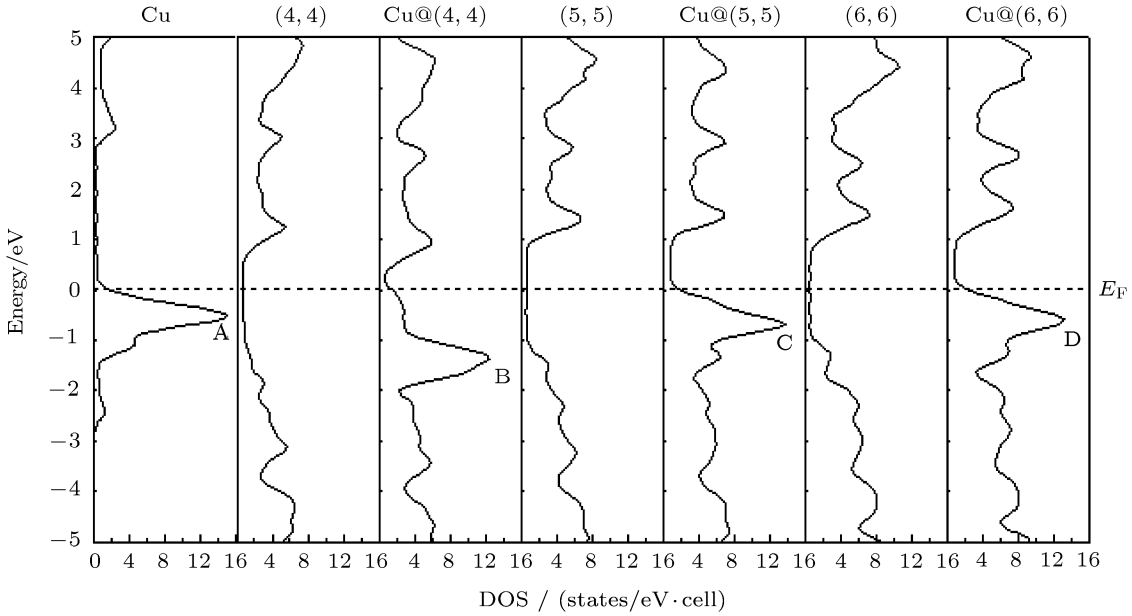


Fig.5. Densities of states (DOSs) for an isolated Cu chain, (4, 4), (5, 5), (6, 6) carbon nanotubes and the Cu@(4, 4), Cu@(5, 5), Cu@(6, 6) combined systems. The Fermi level E_F is set to be at zero energy and is indicated by the dashed line.

4. Conclusions

In the GGA, both the binding and electronic properties of a single copper atomic chain wrapped in (4, 4), (5, 5) or (6, 6) armchair CNTs are investigated by using the first-principles PAW potential within the DFT framework. The following conclusions are obtained.

(i) The positive energies of the Cu@(4, 4) and Cu@(5, 5) combined systems reflect the fact that the (4, 4) and the (5, 5) CNTs are too narrow to wrap a single Cu chain, but the (6, 6) nanotube is nearly ideal to wrap a single Cu chain, especially on its centre axis. We expect that more than one Cu atomic chain would be pulled spontaneously into wider nanotubes by forces amounting to a fraction of a nanonewton.

(ii) The appearance of the charge densities between the Cu chain and the carbon nanotube indicates that the armchair CNTs do not act as "perfectly inert" containers for the Cu chain. Although the nanotube–Cu interaction decreases with the increasing diameter of the CNTs, even in the Cu@(6, 6) system, the charge density does not show complete superposition of those of a pristine (6, 6) carbon nanotube and Cu chain, reflecting the fact that a very weak interaction still exists between the components of the combined system.

(iii) Successively reducing the restrictions of (4, 4), (5, 5) and (6, 6) CNTs on the Cu chain leads to a reduction in shift of the highest peak of the Cu chain towards lower energies, that is from −0.5177 eV of an isolated Cu chain to −1.36785 eV, −0.668 eV and −0.588 eV for the Cu@(4, 4), Cu@(5, 5) and Cu@(6, 6) systems, respectively. In reverse, the strong metallic character of the Cu chain also enhances the metallic character of the combined systems so that the original broader pseudogaps of CNTs around the Fermi level change into the narrow pseudogaps of the combined systems.

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