Optical properties of 4 Å single-walled carbon nanotubes inside the zeolite channels studied from first principles calculations

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Received 26 January 2003
Published online 11 April 2003 – c⃝ EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2003

Abstract. The structural, electronic, and optical properties of 4 Å single-walled carbon nanotubes (SWNTs) contained inside the zeolite channels have been studied based upon the density-functional theory in the local-density approximation (LDA). Our calculated results indicate that the relaxed geometrical structures for the smallest SWNTs in the zeolite channels are much different from those of the ideal isolated SWNTs, producing a great effect on their physical properties. It is found that all three kinds of 4 Å SWNTs can possibly exist inside the Zeolite channels. Especially, as an example, we have also studied the coupling effect between the ALPO$_4$-5 zeolite and the tube (5,0) inside it, and found that the zeolite has real effects on the electronic structure and optical properties of the inside (5,0) tube.

PACS. 78.67.Ch Nanotubes – 73.22.–f Electronic structure of nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 78.40.Ri Fullerenes and related materials

1 Introduction

In the past decade carbon nanotubes (CNTs) [1–5] had been extensively investigated, which is motivated both by their electrical and mechanical properties as well as by their potential applications in future’s nanostructured materials. For example, nanotubes are ideal model systems for studying the transport of electrons in one dimension. Their unique electronic and mechanical properties are proved to be a rich source of new fundamental physics and also make CNTs promising candidates as nanoscale wires, transistors and sensors.

The single-walled carbon nanotube is the simplest type of carbon nanotubes, discovered first by Iijima group [6] in 1993, which is composed of rolled up 2D-graphite sheet. The carbon atoms on the SWNT are arranged in a helical line around its axis. It is well-known that diameter of the SWNTs strongly affects their physical properties, and it has been proved [7] that the calculated curvature energies are inversely proportional to the square of tube radius. The variation of the band gaps of the semiconducting SWNTs with their radius is found to follow the simple rule based on the zone folding theory only for larger diameter tubes, but to differ from it for the tubes with smaller radius. So, it is greatly interested, both theoretically and experimentally [8–11], to study the physical properties of the SWNTs with possible smallest diameters.

The smallest SWNTs with 4 Å diameter have been recently produced in the 1 nm-sized channels of the ALPO$_4$-5 single crystals (AFI in the zeolite terminology) [12], which have the following possible chiral geometrical structures: zigzag (5,0) (diameter, $d=3.93$ Å), armchair (3,3) ($d=4.07$ Å) and chiral (4,2) ($d=4.14$ Å). For such small nanotubes, their large curvature leads to a hybridization of $\sigma^*$ and $\pi^*$ orbitals [13], which has great effects on their electronic structure. For example, unlike larger diameter SWNTs, which can be either metallic or semiconducting, depending only on their helicity, now the zigzag (5,0) tube becomes a metal. Therefore, it is an interesting and also a great challenge to investigate experimentally and theoretically physical properties of these smallest SWNTs.

It is known that the AFI is a type of microporous crystal with one-dimensional channels packed in hexagonal arrays. Its framework consists of alternate tetrahedra of (ALO$_4$)$^-$ and (PO$_4$)$^+$. The AFI single crystals are transparent from the near infrared to the ultraviolet region. Although the AFI is transparent in the specific frequency range, it does not mean, however, that the AFI has no any effect on the electronic and optical properties of the SWNTs inside it. Therefore, it is interesting to see if the AFI crystal has really significant effects on the physical properties of the smallest SWNTs inside it.

In this paper, we use the first-principles calculation to study the structural, electronic and optical properties of the 4 Å-diameter SWNTs inside the AFI single crystal. The geometrical structures of all isolated three kinds of the smallest tubes are fully relaxed, and compared with other theoretical results [14,15]. Especially, as an example, the effects of the zeolite on the electronic structure and optical absorption of the zigzag (5,0) tube have been studied.

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Table 1. Parameters of three kinds of SWNTs in a 13.726 Å × 13.726 Å × C₁ Å hexagonal supercell. The parameters (a, b, c, α, β, γ) are defined as in Figure 2.

| Tube diameter | lattice constant C₁ | a  | b  | c  | α  | β  | γ  |
|---------------|---------------------|----|----|----|----|----|----|
| (5,0)         | 4.03                | 4.23| 1.397| 1.440| 120.0| 110.9|
| (3,3)         | 4.17                | 2.445| 1.420| 1.429| 116.1| 118.9|
| (4,2)         | 4.24                | 11.204| 1.426| 1.408| 1.432| 113.8| 119.0| 118.7|

2 Computational method and details

The total energy plane-wave pseudopotential method has been used in our calculations within the framework of local density approximation (LDA), in which the exchange-correlation energy of the Ceperley and Alder form [16] was included. The ion-electron interaction is modeled by ultra-soft local pseudopotentials of the Vanderbilt form [17] for the carbon atoms with maximum plane wave cut-off energy of 280 eV. The plane-wave pseudopotential program, CASTEP [18], is used on the selected systems. The tube bundle in the channels of AFI is modeled by using a supercell geometry [13], so that the tubes are aligned in a hexagonal array with the closest distance between the adjacent tubes being 13.726 Å, which is the same as that between the adjacent axis of the AFI channels, and found to be a larger enough to prevent the tube-tube interactions. The space group was P1 for the computational models involved in this paper. Firstly, we optimized the supercell of the SWNTs employing BFGS geometry optimization scheme [19,20], and the Monkhorst-Pack scheme [21] with a distance of 0.04 Å between the sampling points in the reciprocal space. The BFGS scheme allows us to specify constraints on the lattice constants and angles before calculation and optimize the cell during the course of calculation. After the final self-consistency cycle, the remaining forces on all atoms were less than 0.03 eV/Å, and the remaining stress was less than 0.05 GPa. Secondly, the calculations on band structure and optical properties are carried out on the relaxed tube bundles. The calculation of energy band structure in reciprocal space are performed over 21 k points along the tube direction, and in the calculation of the polarized absorption spectra the Monkhorst-Pack scheme with a distance of 0.02 Å between points is used for the sampling of reciprocal space. In addition, we also carry out the same calculations on three kinds of tube bundles by using the Troullier-Martin norm-conserving nonlocal pseudopotentials [22] in the Kleinman-Bylander form [23] for comparison, and found that obtained results by using the two different kinds of methods are equivalent to each other.

Also, in order to understand the effects of the AFI crystal on tubes inside its channels, we modeled the combined structure of the AFI crystal with zigzag (5,0) tubes in its channels as shown in Figure 1. The same lattice constant and symmetry group as those without the AFI crystal are taken for this combined structure, in which the geometrical structures of the zigzag (5,0) tubes had been first relaxed. Here, the reason of selecting zigzag (5,0) tube from the three kinds of SWNTs is because its lattice constant along the tube direction (c = 4.23 Å) is about half that of the AFI crystal (c = 8.484 Å), which makes the AFI structure to match more easily with the zigzag (5,0) tubes in its channels than with other kinds of SWNTs. The total atom numbers in one supercell of the combined structure is 112 (72 for the AFI crystal and 40 for zigzag tube), and so only ultra-soft pseudopotentials can be used in our calculation for this combined structure, taking into account the computational time and cost. The combined structure has been entirely relaxed by the same BFGS geometry optimization scheme.

3 Results and discussions

3.1 Tube bundles (5,0), (3,3) and (4,2)

The obtained structure parameters for the fully relaxed pure tube bundle are shown in Table 1. The radius of each tube is slightly larger than that from an ideal rolling of a graphite sheet, while the lattice constant along the tube axis is smaller than that of a rolled-up graphite. We also calculated the bond lengths of these tubes, and find that the average bond length along the tube axis is