Zr-metal adhesion on graphenic nanostructures

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Our high resolution transmission electronic microscopy studies of multiwall carbon nanotubes show, after the growth of zirconia nanoparticles by a hydrothermal route, the presence of surface Zr, forming an atomically thin layer. Using first-principles calculations we investigate the nature of the Zr–C interaction, which is neither ionic nor covalent, and the optimal coverage for the Zr metal in a graphene flake. This preferred coverage is in agreement with that deduced from electron energy loss spectra experiments. We show also that the amount of charge transferred to the C layer saturates as the Zr coverage increases and the Zr–C bond becomes weaker. © 2008 American Institute of Physics. [DOI: 10.1063/1.2966373]

Carbon nanotubes (CNTs) are among the most important constituent materials in nanotechnology applications.¹ As a result of technological advances in the production and processing of CNT, they are widely used to produce reinforced composite materials, such as ZrO₂/CNT compounds.^{2,3} Notwithstanding remarkable success in fabricating these devices, the atomic processes that govern the adhesion of dopants and their interaction with the native graphene structure are not fully understood.⁴ This is particularly true for the adsorption of Zr, an early transition metal, on CNTs or graphene sheets. It is one of the focal points of this letter to study the Zr–C interaction.

Whereas several groups are interested in the zirconia/CNT composites, the nature of the ZrO₂-CNT interaction has not been clarified. In particular, the existence of Zr–C bond has not been demonstrated to date. Using zirconium as catalyst during nanotube growth leads to nanostructures with zirconia crystals of about 15 Å in size anchored in the outer wall.^{5–7} However, our experiments show that this picture is incomplete and the true situation is more complex and intriguing. The experiments described below show that the Zr–C interaction can play a key role in the growth and anchoring of these particles.

We first show the existence of a Zr layer in the outer part of the CNT walls. When depositing Ti (or Al) on graphite materials, it is known that the formation of carbides is mainly due to the {100} and {110} reactive planes. However, the hexagonal planes are chemically stable compared to the reactive planes at the experimental temperatures studied here. Moreover, in nanotubes, the graphitic basal plane is stable against depositing Ti (even Al) at higher temperatures and under pressure.⁸ Our experimental studies use samples obtained via hydrothermal crystallization of the zirconium hydroxide Zr(OH)₄ in the presence of the multiwall nanotubes (MWNTs).⁹ First, we dissolve the precursor Zr(OH)₄ in distilled water by stirring and the pH is modified to obtain a basic dissolution. Then, we add the nanotubes and ultra-

sonicate the mixture. The Zr(OH)₄ aqueous solution with MWCNT thereby obtained is sealed in a stainless steel Teflon autoclave and is kept at 240 °C for 6 h to carry out the hydrothermal reaction. Finally, we dried the solution in a stove at 70 °C for one day and the final product is characterized. This procedure ensures that the Zr additions would remain on the external part of the CNT walls.

We have performed a detailed structural and morphological characterization of the samples by transmission electron microscopy. The different structures [Fig. 1(a)] are identified with high resolution transmission electron microscope (HRTEM) micrographs. To obtain the HRTEM results, a field emission gun microscope JEOL 2010F was used which works at 200 kV and has a point resolution of 0.19 nm. Electron energy loss spectra (EELS), obtained with a Gatan Image Filter (GIF 2000) coupled to the microscope, have an energy resolution of 1.2 eV. In order to improve the chemical analysis, we carried out high angular annular dark field scanning transmission electron microscopy (STEM) on our samples. In the HRTEM image of the ZrO₂/CNT composite, Zr carbide formation by the chemical reaction between Zr and CNT is not observed.

The HRTEM images taken in the nanoparticles attached to the CNT show the characteristic features of the ZrO₂ spectrum, proving that they are indeed zirconia particles. However, something interesting is observed in the areas apparently not covered. In Fig. 1(b), we display the EELS along a section of the wide MWNTs. The spectra show a small peak corresponding to Zr on the walls, without the presence of oxygen or iron (see caption). A deconvolution of the spectra along the line is given in panel (c). To obtain the Zr/C(surface) ratio, we multiply by the averaged number of carbon atoms of the MWNT section (assuming ten layers). The proportion of Zr (ranging from 10% to 20%) is low compared with surface C, and it is clearly larger than the average number of vacancies on the surface of MWNTs. There is always an appreciable concentration of Zr on the C plane, but the Zr/C(surface) ratio is clearly lower than 50%. The interplay among Zr–Zr, Zr–C, and C–C interactions explains this limit. We shall return to this below.

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FIG. 1. (Color online) (a) STEM image of CNT in a region free of zirconia particles. The bright spot enclosed by the CNT is a catalyst particle composed of iron. The top finger structure are MWNTs with 10–20 layers. Across the dashed line we obtain the EELS on transmission shown in part (b). The beam is 0.2 nm wide and a spectrum is measured every 2.5 nm. The vertical dashed-red lines show transitions corresponding to the elements that are expected to be present in the sample. Neither iron or oxygen are present. Notice, however, the large Zr content. (c) Zr/C(surface) distribution profile on the tube, along the same dashed line in panel (a).

We next turn to the Zr–C adsorption. We have investigated a number of adsorption sites and coverage on graphene sheet—stable “graphitic basal plane”—which is a good approach for the surface of wide MWCNTs such as those found in our sample.

We have carried out spin-density-functional calculations using the SIESTA code.¹⁰ The generalized gradient approxi-

FIG. 2. (Color online) Geometries for different Zr/C coverage ratios. Below each configuration, the total energy difference with respect to the ground state for each coverage is given in eV. Carbon atoms are small-dark circles and zirconium ones are large light. The results for the 4×4 cell are not shown because the same total energy differences are obtained for Zr/C=5.6%.

mation for the exchange and correlation follows the Perdew–Burke–Ernzerhof approach.¹¹ The explicit treatment of electronic core states is avoided by using the pseudopotentials of Troullier–Martins.¹² The basis set is double- ζ polarized and includes the $4p$ semicore electrons of Zr. The calculations are done using 3×3 and 4×4 graphene supercells containing 18 and 32 carbon atoms with different zirconium coverages as shown in Fig. 2, ranging between 5.6% and 50%. The Zr atoms are arranged at hollow, bridge, and top positions, in clustered and homogeneous geometries. We used 40 k -points in the irreducible Brillouin zone and a mesh cutoff of 180 Ry that guarantees an energy convergence below 10 meV/atom. We fully relax the atomic coordinates and cell vectors until the forces are lower than 0.04 eV/Å. Then, the binding energy E_B per Zr atom covering the C plane is calculated as

$$E_B = -\{E_T[\text{Zr} - \text{graphene}] - E_T[\text{graphene}] - NE_T[\text{Zr}]\}/N, \quad (1)$$

where $E_T[\text{system}]$ is the total energy of the system and N is the number of Zr atoms per cell.

We first investigate Zr on graphene for low coverage Zr/C ratios of 5.6%. We find that the hollow position for a Zr atom is more stable than top and bridge ones by only 0.74 and 0.82 eV, respectively.¹³ Thus, the barrier between hollow states is at least 0.74 eV, and there could be some diffusion at room temperature. The binding energy per Zr atom is 3.06 eV in the hollow position.

For high coverages (Zr/C=50%), we found the reverse order between the hollow and top positions. For high coverages, the binding energy of hollow Zr with C is 4.66 eV and lower than the binding energy of top Zr which is 5.20 eV. Hence, if we compared with the Zr binding we find in the fully relaxed hexagonal Zr plane, 5.40 eV, we conclude that the binding energy of Zr is larger with nearest-neighbor zirconium atoms than with the graphene sheet. The Zr overlayer

FIG. 3. Charge transfer vs Zr/C coverage ratio. All Zr/C coverage ratios are for hollow positions except the point with a Zr/C coverage ratio of 37.5%, which is a mixed hollow/top configuration.

is under compressive stress at such large coverages. We have also examined at higher Zr/C ratios and find that the graphene layer breaks and forms carbides.

The height of the Zr atoms over the graphene plane strongly increases with the Zr coverage in the case of hollow positions, while remaining almost constant for top positions (2.24 Å for Zr/C=5.6% and 2.38 Å for Zr/C=50%). In hollow positions the height of Zr atoms to graphene plane at low coverages contrasts with that at high coverages. For low coverages, Zr lies tightly bound to C with a Zr–C height of 1.89 Å. In contrast, for high coverages, Zr lies weakly bound to C with a height of 2.61 Å.

We suggest a candidate for optimum coverage with mixed top and hollow positions (2 top/1 hollow) and a Zr/C ratio of 37.5%, as seen in Fig. 2. We find its binding energy per Zr to be 6.08 eV, which is more stable than previous cases by 0.68 eV. This coverage seems to be the optimal one and is slightly larger than the one found in the previous experimental data, in the range of 10%–20% but smaller than 50%.

We next explain the bonding mechanism as a function of the coverage. It has been found for metals on graphitic nanostructures that the metals transfer charge to the hexagonal C cage.^{4,14} Using Mulliken population analysis we compute the charge in the atoms as shown in Fig. 3. We find that the Zr atoms lose charge to the C atoms and the charge transfer per Zr atom decreases as coverages increases, while the extra charge per C is almost constant. In other words, the graphene plane accepts a maximum of electrons when Zr coverage is increased. According to similar analysis for all configura-

tions (top, hollow, and bridge) at each coverage, the differences in the values of charge transfers are around 10%. Clearly, this means that our conclusions slightly depend on the configuration. Finally, we point out that in every case the charge transfer moves from 5s orbitals of Zr to 2p_z orbitals in graphene. We also find that this charge is delocalized in graphene.

In summary, we have found that Zr covers the wall of CNTs during the growth of ZrO₂ nanoparticles using a hydrothermal route. *Ab initio* calculations give a preferred Zr/C coverage ratio of 37.5% in good agreement with the EELS experiments. Here, the Zr atoms are both on top and hollow positions. This might prove important to understand the interaction of transition metals with CNTs and, in particular, the growth mechanism of ZrO₂ nanoparticles for technological applications.

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¹S. Ijima, *Nature (London)* **354**, 56 (1991).

²G. L. Hwang and K. C. Hwang, *J. Mater. Chem.* **11**, 1722 (2001).

³E. Flahaut, A. Peigney, Ch. Laurent, Ch. Marliere, F. Chastel, and A. Rousset, *Acta Mater.* **48**, 3803 (2000).

⁴J. I. Martínez, M. J. López, and J. A. Alonso, *J. Chem. Phys.* **123**, 074303 (2005).

⁵F. Lupo, R. Kamalakaran, C. Scheu, N. Grobert, and M. Rühle, *Carbon* **42**, 1995 (2004).

⁶L. Huang, S. P. Lau, Y. B. Zhang, B. K. Tay, and Y. Q. Fu, *Nanotechnology* **15**, 663 (2004).

⁷Y. Shan and L. Gao, *Nanotechnology* **16**, 625 (2005).

⁸T. Kuzami, O. Ujie, H. Ichinose, and K. Ito, *Adv. Eng. Mater.* **2**, 416 (2000).

⁹N. Garmendia, L. Bilbao, R. Muñoz, L. Goikoetxea, A. García, I. Bustero, B. Olalde, N. Garagorri, and I. Obieta, *Key Eng. Mater.* **361**, 775 (2008).

¹⁰J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejon, and D. Sánchez-Portal, *J. Phys.: Condens. Matter* **14**, 2745 (2002).

¹¹J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

¹²N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).

¹³We are commenting only energies from the ground state energy and its energy differences with the first low lying configuration. These are robust and large enough so that the basis set superposition error would not change the trends. Other configurations are almost degenerate and we are not commenting on them.

¹⁴E. Durgun and S. Ciraci, *Phys. Rev. B* **74**, 125404 (2006).