

## Work functions of pristine and alkali-metal intercalated carbon nanotubes and bundles

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The work functions (WF's) of single-walled carbon nanotubes and bundles are studied using first-principles methods. For individual metallic tubes, the WF is independent of the chirality and increase slightly with tube diameter. For semiconducting tubes, the WF (as defined by the HOMO energy) decreases rapidly. The WF of nanotube bundles ( $\sim 5$  eV) shows no clear dependence on the tube size and chirality, slightly higher than individual tubes. For both metallic and semiconducting nanotubes, the WF decreases dramatically upon alkali-metal intercalation. The electronic states near the Fermi level are significantly modified and the metallic and semiconducting tube bundles become indistinguishable.

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The work function is one of the critical quantities in understanding the field emission properties of carbon nanotubes.<sup>1–5</sup> Although the work function can be estimated from the field-emission spectra based on Fowler-Nordheim model,<sup>3,4</sup> the results are not reliable due to the uncertainty of the local geometry of nanotubes.<sup>4</sup> Other experimental measurements on work functions of both single-walled nanotubes (SWNT's) and multiple-walled nanotubes (MWNT's) included ultraviolet photoemission spectroscopy (UPS) (Refs. 6–11) and transmission electron microscopy.<sup>12</sup> It was found that the work functions of MWNT's are about 0.1–0.2 eV lower than that of the graphite,<sup>6,7,10,12</sup> while the SWNT bundles have slightly higher work functions.<sup>8,9</sup> Upon Cs intercalation the work functions of carbon nanotubes are reduced dramatically,<sup>9,11</sup> which leads to a significant enhancement in field emission.<sup>5</sup> Up to now, theoretical works were only limited to a few nanotubes with finite lengths.<sup>13–15</sup> In this paper, we report results of first-principles calculations on the work functions of individual carbon nanotubes and nanotube bundles. The effects of tube diameter, chirality, and alkali-metal (K, Rb, Cs) intercalation are investigated.

The work function of a bulk metal is related to its Fermi energy  $E_F$  by  $WF = \phi - E_F$ , where  $\phi$  is the electrostatic potential caused by “spilling out” of electron density at the metal surface.<sup>16–18</sup> For those metals with low electron density such as K, Rb, Cs, it is known that  $\phi$  is much smaller than  $E_F$ .<sup>16,17</sup> For carbon nanotubes, the conduction electron density is much smaller than that of K or Cs.<sup>19</sup> In this work, we approximate the WF by the Fermi energy  $E_F$ .<sup>13,14</sup> To determine the Fermi level of carbon nanotubes with respect to the vacuum level, we perform all electron LCAO calculations based on the density functional DMOL package.<sup>20</sup> The density functional is treated by the generalized gradient approximation (GGA) (Ref. 21) with the exchange-correlation potential parametrized by Wang and Perdew (PW91).<sup>22</sup> For the infinite nanotubes, one-dimensional (1D) periodic boundary condition is applied along the tube axis. The Brillouin zone is sampled by large sets of Monkhorst-Pack  $\mathbf{k}$  meshes.<sup>23</sup> (Along the tube axis, 40  $\mathbf{k}$  points are used for standard calculations and 160 points for accurate electronic density of states.) Benchmark calculations are carried out on several alkali metals solids and the graphite. The ionization potential

of a  $C_{60}$  cluster is also calculated from the total energy difference between the neutral and the charged cluster. As shown in Table I, the overall agreement between theory and experiments<sup>8,9,24,25</sup> for different systems is reasonable.

We first address the work functions of individual metallic SWNT's of infinite length, with diameters ranging from 5.7 to 16.3 Å. Both the armchair ( $n,n$ ) and the zigzag ( $n,0$ ) ( $n=3m$ ) chirality are considered. The calculated WF's are summarized in Fig. 1 and Table II. One can see that the WF's for metallic SWNT's fall in a narrow distribution, ranging from 4.63 to 4.77 eV. Careful examinations show that the WF decreases slightly with diameter ( $D$ ) (Fig. 1). Extrapolation towards larger radius limit gives a  $WF_\infty$  of 4.83 eV, close to our calculated value for the graphite (4.91 eV). It is worthy to note that the WF's of both the armchair and the zigzag tubes fit the same linear dependence (Fig. 1), indicating that the WF's of metallic nanotubes are independent of chirality.

For the purpose of comparison, we define the WF of semiconducting tube as the highest occupied molecular orbital (HOMO) energy. The calculated WF's of the semiconducting tube are substantially higher than the metallic ones (Fig. 1). It decreases linearly with  $1/D$  and approaches an extrapolation limit 4.73 eV at  $D \rightarrow \infty$ . The strong diameter dependence can be attributed to the well-known decrease of semiconducting gap with the tube diameter.<sup>26</sup> As far as we know, there is no direct experimental measurement on the work functions of individual SWNT's. But recent experiments on the MWNT tips suggest that the WF's of semiconducting tubes ( $\sim 5.6$  eV) are high than those of metallic ones ( $\sim 4.6$ – $4.8$  eV).<sup>12</sup>

We now discuss the work functions of the nanotube bundles. The bundles are modeled by two-dimensional hexagonal lattices of uniform SWNT's.<sup>27</sup> For all the metallic nanotube bundles studied, the calculated work functions are around 5 eV (see Table II), slightly higher than individual tubes and the graphite. The increase of WF's in tube bundles can be understood by the tube-tube interaction.<sup>28</sup> Our theoretical results agree well with the UPS experiments, which suggested the work functions of SWNT bundles to be 4.8 eV (Ref. 8) or 5.05 eV.<sup>9</sup>

TABLE I. Work function of bulk alkali metals (K, Rb, Cs) (Ref. 24), graphite (Refs. 8 and 9), nanotube bundle (see Table II and discussions in text) (Refs. 8 and 9), and the ionization potentials of  $C_{60}$  cluster (Ref. 25). GGA denotes present GGA calculations, “Exp.” are the experimental WF values (Refs. 8,9,24,25). All units are in eV.

	K	Rb	Cs	graphite	nanotube	$C_{60}$
WF (GGA)	2.69	2.42	2.31	4.91	$\sim 5.0$	7.87
WF (Exp.)	2.30	2.16	2.14	4.8 (Ref. 8), 4.6 (Ref. 9)	5.05 (Ref. 8), 4.8 (Ref. 9)	7.61

In addition to pristine materials, the electronic properties of carbon nanotubes can be efficiently controlled by alkali-metal intercalations.<sup>29–33</sup> Recently, nanoelectronics devices have been constructed on the basis of alkali-metal doped carbon nanotubes.<sup>34</sup> Thus, it is important to investigate the effect of alkali-metal intercalations. We have carried out systematical calculations on the effect of intercalations in both metallic (10,10) and semiconducting (17,0) tubes bundles. Intercalation density up to  $K_{0.1}C$  (Rb, Cs) (close to the saturation density in nanotube bundles<sup>29</sup> and the graphite<sup>35</sup>) are studied. Both the inside of SWNT’s and the interstitial sites are explored. The initial configurations of alkali-metal atoms are chosen to maximize the ion-ion distance.<sup>27</sup> Structural relaxations find no significant change from the initial configurations. For a given intercalation concentration, the WF is insensitive to the detailed configurations of the intercalated atoms. The lattice constants of two-dimensional hexagonal lattices are expanded. For example, we find that the intercalations of K atoms into the interstitial sites of (10,10) tube bundle can induce about  $\sim 2$  Å lattice expansion, which is comparable to expansion of 1.95 Å in K intercalated graphite<sup>35</sup> and 1.85 Å in the  $HNO_3$  intercalated SWNT bundles.<sup>36</sup>

Figure 2 shows the calculated work functions of intercalated tube bundles as functions of the metal concentration for various alkali metals. In general, the work function dramatically decreases with small amount of intercalations. The reduction becomes much slower at higher intercalation density. Furthermore, there is almost no difference between the WF’s of intercalated (10,10) and (17,0) tube bundles. Thus, one can associate a single value of work function to a nanotube bundle with mixed metallic and semiconducting tubes. The WF for Cs-doped bundles is slightly lower than that of the Rb- or K-doped systems. The trend is consistent with the WF of bulk metals [ $WF(K) > WF(Rb) > WF(Cs)$ , see Table I]. The reduction of work function upon increased Cs-intercalation density in our calculations was observed in recent experiments by Suzuki *et al.*<sup>9</sup> However, the experimental WF at highest Cs concentration (about 2.0 eV) is higher

TABLE II. Work function (eV) of individual metallic tubes and ropes (tube bundle) with various diameters and chirality ( $m, n$ ) obtained from GGA calculations.

$(m, n)$	(5,5)	(6,6)	(12,0)	(8,8)	(15,0)	(10,10)	(12,12)
tube	4.68	4.71	4.73	4.74	4.73	4.76	4.77
rope	5.08	5.07	5.05	5.00	4.98	5.01	4.94

than our calculated value (about 3.4 eV). This discrepancy might be understood by the WF of bulk Cs metal (about 2.14 eV, see Table I). At high density Cs may form atomic layers on the surface of nanotube bundles. Similar effects were observed in K adsorption on graphite surface, where the WF initially decreases with increasing metal coverage before attaining the WF of the alkali metal.<sup>37</sup>

Intuitively, the reduction of WF’s can be understood by the charge transfer from metal to carbon nanotube, which shifts the Fermi level of conduction band towards the vacuum. Experimentally, the charge transfer from metal atoms to the nanotube have been confirmed by the resistances<sup>30,31</sup> and Raman spectra.<sup>32</sup> However, our present results show that interaction between K (or Rb, Cs) and nanotube cannot be simply described by a rigid band model with charge transfer. Shown in Fig. 3 are the electronic density states for pristine and K-intercalated (10,10) SWNT bundles. Similar to the case of Li intercalation,<sup>27</sup> the valence bands are almost not affected by K intercalations. In contrast, the conduction bands are significantly modified by potassium-carbon interactions. New peaks associated with alkali-metal atoms are found in the conduction bands. The density of states near the Fermi level is greatly enhanced by the contributions of alkali metals. Our theoretical results are supported by recent experiments on the optical properties of

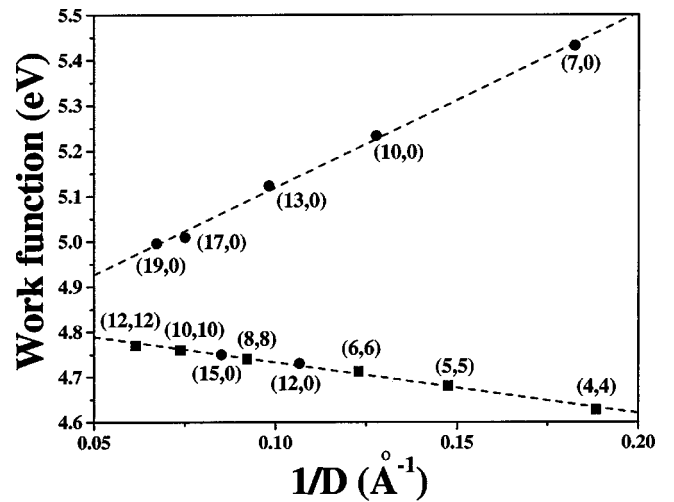


FIG. 1. Work functions (eV) of individual metallic and semiconducting SWNT’s vs the inverse tube diameter  $1/D$  (squares: armchair SWNT’s; dots: zigzag SWNT’s). Linear extrapolation towards the  $D \rightarrow \infty$  limit yields  $WF_\infty$  of 4.84 eV for metallic tubes and 4.73 eV for semiconducting ones, close to the calculated value (4.91 eV) for graphite.

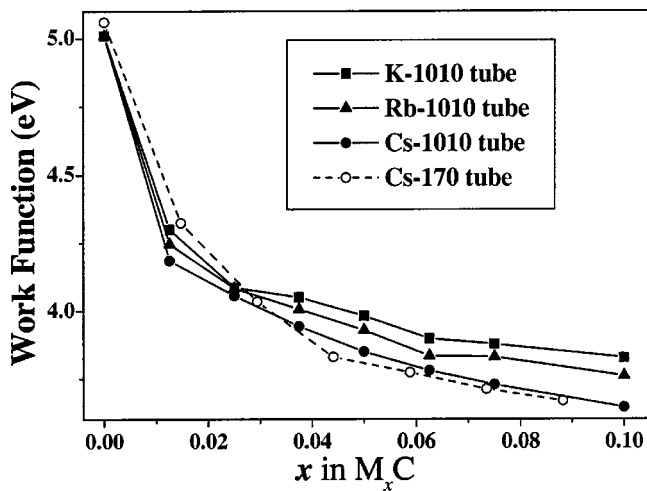


FIG. 2. Work functions (eV) of alkali-metal intercalated carbon nanotube bundles vs the intercalation density ( $x$  in  $M_xC$ ,  $M$  denotes metal). Initially, the work function decreases dramatically with intercalation density. The reduction becomes much slower at higher density.

the K and Cs intercalated nanotube bundles.<sup>33</sup> In addition, we have also investigated the intercalated semiconducting bundles. The density of states at Fermi level for the metallic and semiconducting bundles become comparable. This is consistent with recent NMR measurements on K-intercalated SWNT bundles.<sup>38</sup>

In summary, we have performed first principles calculations on the work functions of pristine and intercalated SWNT nanotube and bundles. The WF's of metallic nanotubes weakly depend on the tube size and are comparable to

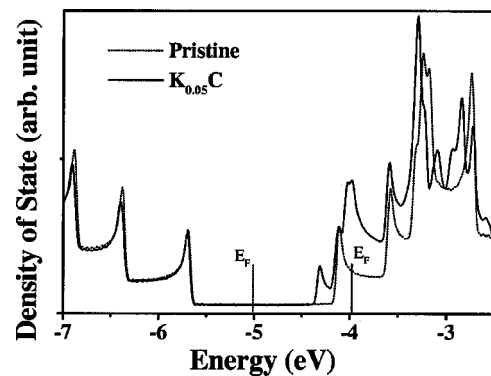


FIG. 3. Electronic density of states of pristine (dotted line) and K-intercalated (solid line) (10,10) SWNT bundles ( $K_{0.05}C$ ). The valence bands of nanotube are almost not affected by K intercalations, while the conduction bands are significantly modified by the potassium-carbon interactions.

the graphite. The work functions of all the metallic tube bundles are around 5 eV, slightly higher than those of individual tubes. Upon alkali-metal intercalation, the WF's of tube bundles decrease dramatically and the electronic states near Fermi level are significantly modified. The work functions and density of states at Fermi level become indistinguishable for metallic and semiconducting tubes bundles.

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