# Modulation of the work function of fullerenes $C_{60}$ and $C_{70}$ by alkali-metal adsorption: A theoretical study

Hong Liang [a], Shunfu Xu [a,b,*], Weihui Liu [b], Yueqiang Sun [a], Xiangfa Liu [a], Xinqing Zheng [a], Sen Li [a], Qiang Zhang [a], Ziliang Zhu [a], Xiaochun Zhang [a], Chengguo Dong [a], Chun Li [b], Guang Yuan [b,c], Hitenori Mimura [b]

[a] *Institute of Architecture and Engineering, Weifang University of Science and Technology, Weifang 262700, China*
[b] *Department of Physics, Institute of Information Science and Engineering, Ocean University of China, Qingdao 266100, China*
[c] *Research Institute of Electronics, University of Shizuoka, Hamamasu 432-8011, Japan*

## ABSTRACT

The impact of alkali-metal (Li/Na/Cs) adsorption on work function of fullerenes $C_{60}$ and $C_{70}$ was investigated by first-principles calculations. After adsorption, the work functions of fullerenes $C_{60}$ and $C_{70}$ decrease distinctly and vary linearly with the electronegativity of the alkali metal elements, and the positions where the alkali atoms are adsorbed considerably influence the work functions. On the contrary, a vacancy defect elevates the work functions of the fullerenes $C_{60}$ and $C_{70}$. The variation in the work functions rests with variation in Fermi level (which are attributed to charge transfer) and variation in vacuum levels (which are attributed to the induced dipole moments). Moreover, alkali-metal adsorption can also improve the electric conductivity of a fullerene mixture of $C_{60}$ and $C_{70}$.

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## 1. Introduction

$C_{60}$, a fascinating molecule formed as a truncated icosahedron with 20 hexagonal and 12 pentagonal faces, and 60 vertices, was discovered by Kroto et al. [1] in 1985. Since then, a new form of pure carbon, called fullerene [2], has received considerable attention as potential candidates for future nanoelectronics and has been extensively studied. $C_{60}$ represents the most identifiable member of the first molecular carbon allotrope existing in universe long before it was discovered. Different kinds of the fullerenes, in the form of $C_{60}$, $C_{70}$, $C_{76}$, $C_{82}$ and $C_{84}$ molecules, were found in a family of minerals known as shungites [3].

Field emission characteristics and electronic structures of $C_{60}$ molecules were investigated experimentally by Lin et al. [4]. The work function of $C_{60}$ polycrystal films is about 4.69–4.72 eV, which is close to the work function of graphene [5]. Hebard et al. [6,7] found that $C_{60}$ and $C_{70}$ become conductive when doped with alkali metals, and potassium-doped $C_{60}$ can act as a high-temperature superconductor at 18 K.

The first-principles calculations indicated that the work functions of $(5,5)/(9,0)$ single-walled carbon nanotube with a capped edge can be distinctly modulated by alkali-metal adsorption, and electronegativity of the alkali atom plays a dominant role in the work functions of adatom–fullerene systems [8–10]. However, issues regarding the field emission characteristics of fullerenes with alkali-metal adatoms remain. In this Letter, we report the results of work functions in the axial and radial directions of fullerenes ($C_{60}$ and another fairly common fullerene: $C_{70}$) with different alkali-metal adatoms (Li/Na/Cs) based on first principles calculations. The calculation results show that the electronegativity of the alkali metals is crucial in manipulating the work functions of fullerenes $C_{60}$ and $C_{70}$. The effect of vacancy defect and adsorption position of different alkali metals on the field emission characteristics of fullerenes is also investigated.

## 2. Calculation details

Fig. 1 shows theoretical models of the selected fullerenes $C_{60}$ and $C_{70}$. A vacancy defect was made by removing a carbon atom from the tip (pentagon or hexagon) of the fullerenes $C_{60}$ and $C_{70}$ (which was labeled as T in Fig. 1(a)–(b)). An alkali-metal adatom (Li/Na/Cs) was initially located above the center of the pentagons or hexagons (which was labeled as $P_1$–$P_4$ in Fig. 1(a) for the $C_{60}$ and in Fig. 1(b) for the $C_{70}$) for the perfect fullerenes (P-fullerene),
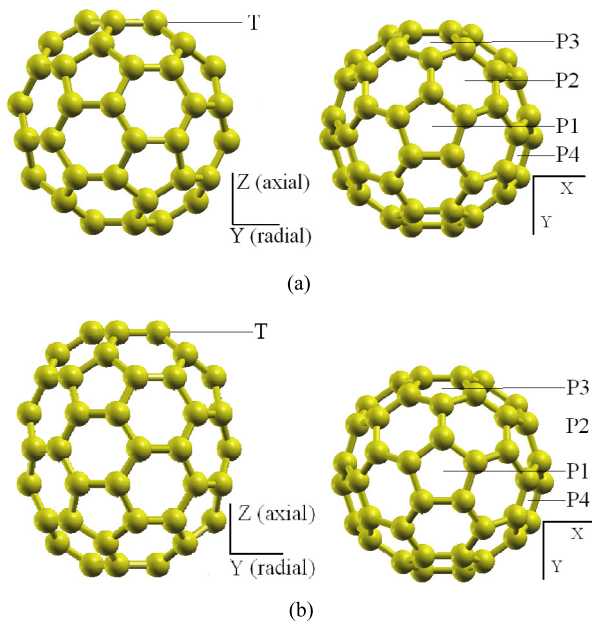
**Fig. 1.** Side and top views of (a) perfect fullerene $C_{60}$ and (b) perfect fullerene $C_{70}$ marked with the adsorption position $P_1$–$P_5$ and defect position T.

and nearby the vacancy defect for the defective fullerenes (D-fullerene). The axial and radial directions of the fullerenes and the $X/Y/Z$ axis were defined in Fig. 1.

Our calculations were performed within first-principles DFT (density functional theory) under GGA (generalized gradient approximation) of Perdew, Burke, and Ernzerhof (PBE) [11]. The energy cutoff in the plane-wave basis set is 30 Ry. Ultra-soft pseudopotentials (USPP) are used to describe the valence electrons interaction with the ion cores. The Brillouin zone was sampled using the $\Gamma$ point approximation. The atomic positions were optimized until all components of all force was less than $1.0 \times 10^{-4}$ a.u. The fullerenes $C_{60}$ and $C_{70}$ were constructed within the same tetragonal supercell with a vacuum width of 30 Å in the axial direction and 20 Å in the radial direction to avoid interactions between adjacent fullerenes. The adatom–graphene system lacks inversion symmetry and therefore has a net electric-dipole moment perpendicular to the surface. To remove spurious dipole interactions between periodic images along the $Z$ direction, we applied corrections to the local electrostatic potential and the total energy (Dipole and potential correction (DPC) method by Neugebauer et al.) [12,13]. The work function $W_F$ was defined as the minimum energy which was necessary to extract an electron far from Fermi level into the vacuum level

$$W_F = \phi - E_f$$

where $\phi$ represents the vacuum level and $E_f$ represents the Fermi level. The vacuum level was determined by the electrostatic potential in the vacuum region, and was a sufficient distance from the fullerenes $C_{60}$ and $C_{70}$ in the $Z/X$ direction that the value converged. All the calculations were performed using the PWscf code in the Quantum ESPRESSO suite [14,15].

## 3. Results and discussions

According to the present calculations, the work function of the P-fullerene $C_{60}$ along the axial/radial direction ($Z$-axis/$X$-axis, $Z$-$W_F$/$X$-$W_F$) is 5.02/5.02 eV, and the $Z$-$W_F$/$X$-$W_F$ of P-fullerene $C_{70}$ is 5.00/5.00 eV. In contrast, the work function of the D-fullerene $C_{60}$ along the axial/radial direction ($Z$-axis/$X$-axis, $Z$-$W_F$/$X$-$W_F$) is 5.12/5.11 eV, and the $Z$-$W_F$/$X$-$W_F$ of D-fullerene $C_{70}$ is
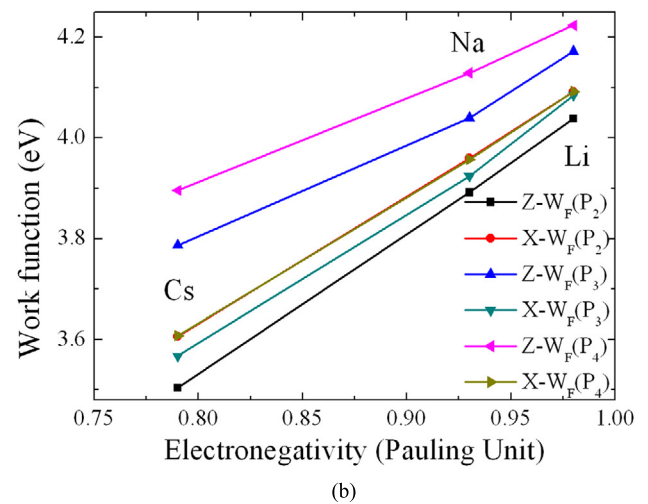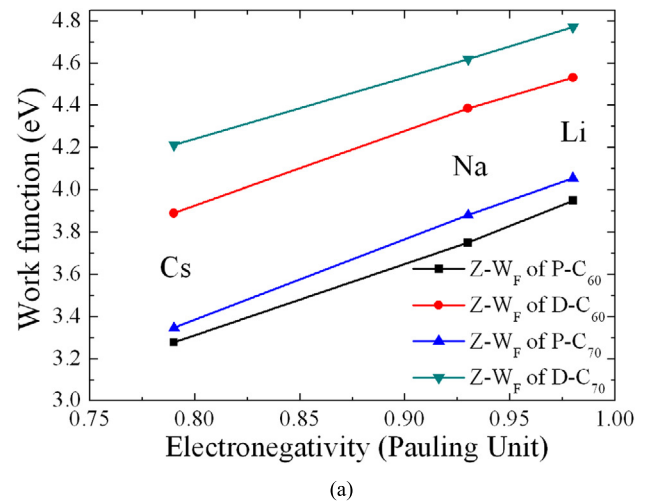


**Fig. 2.** (a) Axial work functions of P- and D-fullerenes with Li/Na/Cs on $P_1$ vs. electronegativity. (b) Axial and radial work functions of the P-fullerene $C_{60}$ with Li/Na/Cs on $P_2$–$P_4$ vs. electronegativity.

5.26/5.25 eV. The difference is derived from the orientation of the alkali-metal adatoms and the distribution of the carbon atoms. As an example, the tip of the D-fullerene $C_{60}$ is more sharp and the distance between the two adjacent carbon layers is less than that of the P-fullerene $C_{60}$, which builds up the capability of binding electrons for the D-fullerene $C_{60}$. Therefore, the work functions of the D-fullerenes are slightly higher than that of the P-fullerenes.

After alkali-metal adsorption, the work functions of all the P-fullerenes and D-fullerenes along the $Z$-axis and the $X$-axis decrease significantly. The $Z$-$W_F$/$X$-$W_F$ of the P- and D-fullerene $C_{60}$ with alkali-metal adatoms are lower than that of the P- and D-fullerene $C_{70}$ with the same adatoms. However, the $Z$-$W_F$/$X$-$W_F$ of the D-fullerenes with alkali-metal adatoms are higher than that of the P-fullerenes with the same adatoms. The $Z$-$W_F$ and $X$-$W_F$ correspond with the work functions of fullerenes with alkali-metal adatoms on their surface and in their grooves, respectively.

Fig. 2(a) summarizes the axial work functions of P- and D-fullerenes $C_{60}$ and $C_{70}$ with alkali-metal adatoms on $P_1$ plotted against the electronegativity of the alkali metal elements. All the work functions of fullerenes increase linearly with the electronegativity of the alkali metal elements. Table 1 lists the slopes of these linear curves. The slopes are comparable with that of the Gordy–Thomas equation ($W_F = 2.3\chi + 0.34$) [16,17], which is a linear relationship between the work functions and electronegativity. The slopes of the $X$-$W_F$ are more consistent with the Gordy–Thomas