Regular article

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Study of Pb ion adsorption on (n, 0) CNTs (n = 4, 5, 6)

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Abstract: Adsorption of Pb ion on the (n, 0) carbon nanotube (CNT) (n=4, 5, 6) surface, pure and defected with single vacancy, is investigated based on density functional theory. Pristine (n, 0) CNTs can produce a certain degree of chemical adsorption of Pb ion. While a single vacancy is introduced, the adsorption ability of CNTs for Pb ion increases greatly, and the band gap changes significantly before and after adsorption. SV-(6, 0) CNTs have the strongest adsorption ability, and SV-(5, 0) CNTs are the potential material for the Pb ion detection sensor. It is expected that these could be helpful to the design of Pb filters and sensors.

Keywords: adsorption; carbon materials; nanotubes; Pb ion.

1 Introduction

Lead is a dangerous heavy metal contained in water, which is not biodegradable in water. High accumulation of lead in drinking water causes anemia, cancer, renal

kidney disease, nervous system damage and mental retardation [1–3]. A number of methods have been developed for the detection and removal of lead from water [4–6]. Among those methods, adsorption is confirmed to be an economical and effective method for the removal of lead from water [7, 8].

In recent years, as a new type of nanomaterial with strong abilities of adsorption and desorption, carbon nanotubes (CNTs) have been employed extensively as an efficient adsorbent for the detection of harmful gases and removal of heavy metals from aqueous solutions [9–11]. A lot of research results show that the large specific surfaces and low dimensions make CNTs a promising material for manufacturing filters and sensors [12–14]. In previous reports, CNTs have been employed to remove cadmium [15], chromium [16], lead [17–19], nickel [20], copper [21, 22], mercury [23], arsenic [24, 25], zinc [26, 27] and cobalt [28].

Absorption of a Pb atom on the zigzag (10, 0) CNT surface, pure and functionalized with various groups, was investigated based on density functional theory (DFT) [29]. There are still many questions that can be raised. For example, in many cases, lead exists in water as ions, not atoms. Vacancy is a common defect in CNTs, which affects the adsorption performance of CNTs [30]. What is the relationship between Pb ion and vacancy CNTs?

In this paper, the adsorption and electron properties of Pb ion on vacancy-defected single-walled zigzag (n, 0) CNTs (n=4, 5, 6) are studied using the DFT calculations, in order to explore the effects of vacancy on Pb ion adsorption capability of CNTs.

2 Calculation methods and model

We construct a $25 \times 25 \times 8.50$ Å supercell with periodic bounding conditions to avoid the interactions between the neighboring nanotubes [31, 32]. All the calculations are carried with the Demol3 code based on DFT [33, 34]. The generalized gradient approximation with the Perdew-Burke-Ernzer parameterization is used to describe the electronic exchange and correlation effects [35]. Convergence tolerance in energy, max force and max displacement

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are set as 1.0×10^{-5} Ha, 0.002 Ha/Å and 0.005 Å, respectively. The Monkhorst-Pack special k-points are set as $1 \times 1 \times 6$. An energy cutoff of 700 eV is employed [36]. The adsorption energy E_{ad} of Pb ion onto CNTs is defined as $E_{\text{ads}} = E_{\text{(CNTs)}} + E_{\text{(Pb ion)}} - E_{\text{(total)}}$, where $E_{\text{(total)}}$ is the total energy of Pb ion adsorbed on the surface of nanotubes with optimized pure (n, 0) CNTs, S-doped (S-) (n, 0) CNTs, single vacancy defected (SV-) (n, 0) CNTs and S-SV-(n, 0) CNTs. $E_{\text{(CNTs)}}$ is the total energy of optimized pure (n, 0) CNTs, S-(n, 0) CNTs, SV-(n, 0) CNTs and S-SV-(n, 0) CNTs. $E_{\text{(Pb ion)}}$ is the energy of isolated Pb ion. The greater the value of E_{ads} , the stronger the adsorption ability.

3 Results and discussions

The optimized structure of single vacancy (SV)-(n, 0) CNTs is shown in Figure 1, which shows that there exist reactive defect edges due to the dangling bonds [37]. We design the possible initial adsorption structures as shown in Figure 1, and get the optimal adsorption configuration of adsorption of Pb^{2+} -SV-(n, 0) CNTs which has the greatest adsorption energy. Then we design the adsorption of Pb ion on pure (n, 0) CNTs, as presented in Figure 2. Before adsorption, in the optimized vacancy structure, the C–C bond near the vacancy is elongated, and the three carbon atoms adjacent to the vacancy are recessed toward the center of the tube. When Pb ion is adsorbed, it is approximately on the hollow position of the carbon atom ring. Among the three C atoms adjacent to the Pb ion, the nearest C atom is obviously pulled up to the outside of the tube wall, while

the remaining two C atoms remain certain depression toward the tube center.

The adsorption energy, the energy gaps, the distance between the Pb ion and the nearest C atom, and the charge transfer of the corresponding Pb ion adsorbed configurations are shown in Table 1. In our Pb^{2+} -SV-(n, 0) CNT model, the distance between the Pb ion and the nearest C atom is significantly smaller than the conventional physical adsorption distance [38]. These results indicated that tight binding existed between SV-(n, 0) CNTs and the Pb ion. It is the strong attraction between SV-(n, 0) CNTs and Pb ion that causes the structural changes in SV-(n, 0) CNTs.

Symmetry influences system stability significantly [39, 40], which usually changes the physical properties and chemical properties. Vacancy improves the chemical reactivity of the system through decreasing the symmetry of the initial structure, which is helpful to the adsorption of Pb ion.

The calculated gap energy for all the pure single-walled CNTs is 0 eV. Generally, there exists a rule that the zigzag (n, 0) CNTs with $n \bmod 3 \neq 0$ are semiconductors. However, the gap decreases to 0 (metallic) for (4, 0) and (5, 0) CNTs in our results, which is the same as the reports in [41]. The DFT calculations predict that small-diameter SWNTs are metallic due to hybridization of p and s atomic orbitals. This is due to the $\sigma^*-\pi^*$ hybridization effects caused by the curvature of small-diameter CNTs. In these small-diameter CNTs, the π^* and σ^* states mix and repel each other, leading to lower pure π^* states [42]. While the diameter increases, the calculated result will conform to

Figure 1: The optimized structure of SV-(n, 0) CNTs (n = 4, 5, 6).

Figure 2: The optimized configurations of Pb^{2+} -SV-(n, 0) CNTs (n = 4, 5, 6); the red ball is Pb ion.

Table 1: The adsorption energy (E_{ads}), the energy of band gap (E_g), the interaction distance (D), and the charge transfer from tubes to Pb ion (Q).

Configuration (eV)	E_{ads} (eV)	E_g (eV)	D (Å)	Q (e)
Pb ²⁺ -(4, 0) CNTs	1.822	0	2.685	0.710
Pb ²⁺ -(5, 0) CNTs	2.285	0	2.648	0.787
Pb ²⁺ -(6, 0) CNTs	2.856	0	2.619	0.901
Pb ²⁺ -SV-(4, 0) CNTs	3.808	0	2.478	0.760
Pb ²⁺ -SV-(5, 0) CNTs	6.538	0.156	2.426	0.868
Pb ²⁺ -SV-(6, 0) CNTs	5.166	0.031	2.392	0.949

the rule. For example, our gap value of (8, 0) CNTs reaches 0.63 eV [32], which is very close to the value of 0.56 eV [43]. There are band gap values of 0.019 eV, 0.238 eV, and 0.190 eV for SV-(n , 0) CNTs ($n=4, 5, 6$), respectively, which shows that vacancy increases the energy gap and decreases the conductivity. The results are consistent with the Jahn-Teller effect [44, 45] that the energy gap would vary when the symmetry suffers damage for one-dimensional materials. After adsorption of Pb ion, the energy gaps of three configurations become 0, 0.156 and 0.031 eV.

According to [46], the physical adsorption energy is usually less than 0.2 eV and the chemical adsorption energy is usually larger 0.2 eV. We can see that chemical adsorption exists in (n , 0) pristine carbon tubes, which is the same as in reports in the literature [30], but our adsorption energy is higher than theirs. It is attributed that our research object is Pb ion rather than Pb atom, which itself has stronger chemical activity. In these vacancy-carbon tubes, the adsorption energy and the charge transfer increase dramatically, while the adsorption distance decreases. Among them, the adsorption energy of the SV-(5, 0) CNTs is the largest, reaching 6.528 eV, and the adsorption bond length is 2.392 Å. The

Mulliken population is calculated since the net charge transfer plays an important role in the electronic properties and stability of systems [47]. Electron transfer during the adsorption may cause the electronic structure of the adsorption system to change, and then affect the electrical conductivity of crystal. We find that Pb ion acts as an electron acceptor, and SV-CNTs lose electrons.

We take Pb²⁺-SV-(6, 0) CNT configuration as an example and studied the partial density of states (PDOS) of C and Pb near Fermi level, as shown in Figure 3, where C corresponds to the nearest carbon atom adjacent to the lead ion. From this figure, we could see that the hybrid orbits formed between the C and Pb atom after Pb ion being adsorbed on SV- CNTs. Furthermore, from another point of view, we can also find that the p orbitals of C and s orbitals of Pb both had obvious peaks at -1.9 eV, -2.8 eV and -5.8 eV, which suggested the strong hybridization between the p orbitals of C and s orbitals of C. All these showed a strong interaction between the Pb ion and the C atom of SV-(6, 0) CNTs. Moreover, it is the reason for larger adsorption energy and shorter interaction distance of Pb²⁺-SV-(6, 0) CNTs.

Figure 4 shows the total electron density of Pb²⁺-SV-(6, 0) CNTs. The blue region represents a large density of electrons. The deeper the blue color, the stronger the charge density. The chemical band may be formed in the overlap area of electrons. From this figure, we can see that an obvious overlap area appears between Pb ion and SV-(6, 0) CNTs, which meant that there may exist chemical adsorption. All the analysis above has illustrated that the Pb ion is more preferred to be absorbed on SV-(n , 0) CNTs than the pristine CNTs, and single vacancy can dramatically improve the adsorption activity. Among these small-diameter CNTs, the SV-(6, 0) CNTs have the best adsorption to Pb ion, and the SV-(5, 0) CNTs have the

Figure 3: The PDOS of C and Pb in Pb²⁺-SV-(6, 0) CNTs.

Figure 4: The total electron density of Pb^{2+} -SV-(6, 0) CNTs.

strongest change in energy gap before and after adsorbing Pb ion. The former are suitable for adsorption material, while the latter are a potential material to make the sensor for Pb ion detection.

4 Conclusions

The adsorption energy, changes of surface structure, interaction distance and electronic structure are analyzed to study the Pb ion absorption and sensitivity of various small-diameter CNTs with single vacancy by DFT calculations.

1. Pristine (n, 0) CNTs can produce a certain degree of chemical adsorption of Pb ion. The larger the tube diameter, the stronger the Pb ion adsorption ability.
2. When a single vacancy is introduced, the adsorption capacity of CNTs for Pb ion increases greatly, and the band gap changes significantly before and after adsorption.
3. Among them, SV-(6, 0) CNTs have the strongest adsorption ability, and SV-(5, 0) CNTs are a potential material for the Pb ion detection sensor.

It is expected that these results could provide helpful information for the design and fabrication of the Pb filters and sensors.

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