First-Principles Calculations of the Adsorption Property of C₆H₇N and C₇H₇N on Pd-doped TiO₂ Anatase (1 0 1)

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Abstract

In this work, we proposed a novel Pd-doped TiO₂ anatase (1 0 1), material as the gas sensing material to detect typical lung cancer volatile organic compounds: aniline (C₆H₇N) and o-tolidine (C₇H₇N). After analyse the adsorption structure, charge transfer, the density of states and band structure, it is found that Pd-TiO₂ presents good gas sensing properties to C₆H₇N and C₇H₇N. The single doped Pd atom acts as the active site to interact with the gas molecules, which causes the electron redistribution and the change of conductivity of adsorption system. According to the different change characteristics of conductivity upon different gas molecules adsorption, Pd-TiO₂ material can not only realize high gas sensitivity, but also realizes selectivity to C₆H₇N and C₇H₇N. The calculation results play a guiding role to prepare high-performance Pd-TiO₂ material gas sensor in experiment.

Keywords: Lung cancer; Volatile organic compounds; Pd doping; TiO₂ anatase (1 0 1); DFT method

Introduction

Lung cancer, as a kind of therioma, has been one of the most serious diseases that threaten human life in the world today [1,2]. Influenced by smoking, carcinogen, hazardous air pollutants [3-6], the incidence and mortality of lung cancer are experiencing explosive growth in recent years. According to recent statistics [7-9], both the incidences and mortality of lung cancer for male rank first among all of the therioma. Though the incidence and mortality of lung cancer for female are less than that of male [10], they still ranked in the front. It is urgent to find effective methods to reduce the incidence and mortality. Generally, the patients go to hospital and get formal treatment only after they realize they have already get lung cancer [11,12]. Sometimes it has been got really serious, making them miss the important time to get immediate treatment at early stage. Therefore, developing a portable lung cancer detection device for early prevention and detection can be an optimal method to realize reduce the incidence and mortality, which possesses high-efficiency, flexibility, safety and low-cost with enough detection precision.

There will be lots of symptoms occur along with the occurrence of lung cancer at early stage, such as lung pain, cough and hemoptysis [13]. Based on these symptoms it is feasible to find the effective methods to detect the lung cancer. According to recent studies, the volatile organic compounds of lung cancer patients contain specific gas molecules that can be used to characterize the type and severity of lung cancer [14,15]. However, it is nearly impossible to detect the type and concentration of all volatile organic compounds molecules at the same time. In this study, we chose aniline (C₆H₇N) and o-tolidine (C₇H₇N) as the typical gas molecules to characterize lung cancer due to its universality and high concentration compared with other volatile organic compounds [16].

Due to the high sensitivity, fast repose and flexibility of gas sensors, it has been widely applied in industrial manufacture, environmental monitoring and gas detection[17,18]. While until now, there are no existing sensors that used to detect C₆H₇N and C₇H₇N, nor any studied reported about developing these gas sensors. In order to realize the high-precision detection, it is urgent to studies new gas sensor based on novel gas sensing materials. TiO₂ anatase, a kind of n-type metal transition metal oxide gas sensing material, has attracted widespread attention because of its advantages in low work temperature, low-cost, easy preparation and high stability [19,20]. In this study, TiO₂ anatase (1 0 1), abbreviated to TiO₂, is proposed as the gas sensing material to analyse its adsorption properties and gas sensing mechanism to C₆H₇N and C₇H₇N based on first principle calculations. In addition, Pd single metal doping method has been adopted to enhance its gas sensitivity according to previous research [21-23].

Methods

All of first-principles calculations are carried out on Dmol³ module of Materials Studio, which has been widely used to analyse and predict the properties of materials [24]. First, Pd-TiO₂ (1 0 1), abbreviated to Pd-TiO₂, was built and optimized by substituting one Ti atom with Pd atom on surface. A periodic boundary model with lattice parameters 10.89 Å × 11.33 Å × 19.35 Å was adopted in our work, which is sufficient to avoid the interaction between adjacent gas adsorption structures [25]. Then C₆H₇N and C₇H₇N molecules were built and optimized to reach their most stable structures. Finally, C₆H₇N and C₇H₇N molecules are separately relaxed onto the surface of Pd-TiO₂. In order to ensure the computation accuracy, various approaching manners of C₆H₇N and C₇H₇N molecules were considered to find the lowest energy structures.

The geometry optimization was calculated by Generalized Gradient Approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) [26],...
which possessed high accuracy on calculating the electron-electron exchange and correlation interactions. Spin-polarized density functional theory was applied to deal with the electronic properties calculations of adsorption structures. The calculation parameters of electronic core treatment and basis set were all electrons and Double Numerical plus D-Functions (DND). In order to ensure calculation accuracy, the energy threshold, maximum force and self-consistent field convergence criteria were set as $5.44 \times 10^{-4} \text{ eV}$, $1.09 \times 10^{-1} \text{ eV/Å}$ and $2.72 \times 10^{-4} \text{ eV}$, respectively. Moreover, The Brillouin zone integrations are performed using a $1 \times 1 \times 1$ Monkhorst-Pack mesh in calculations, which is shown to be a good approximation for Pd-TiO$_2$ [27].

When gas molecules interact with the surface of Pd-TiO$_2$, the interaction energy was defined as adsorption energy ($E_{\text{ads}}$), which can be calculated from following equation (1):

$$E_{\text{ads}} = E_{\text{surface/gas}} - E_{\text{surface}} - E_{\text{gas}}$$  \hspace{1cm} (1)

$E_{\text{surface/gas}}$ represents the total energy after gas molecules adsorbed on the surface of Pd-TiO$_2$. $E_{\text{surface}}$ represents the total energy of Pd-TiO$_2$ after reaching the lowest energy state. $E_{\text{gas}}$ is the total energy of isolated gas molecules before adsorption. If $E_{\text{ads}}<0$, the adsorption process is assumed to be exothermic and generally occurs spontaneously.

The electrons redistribute during the gas molecules adsorption process, which directly influence the conductivity of the adsorption system. And Mulliken population analysis is used to assess charge density distribution [28,29]. Then the charge transfer ($Q$) between gas molecule and surface is calculated using the following equation (2), where $Q_{\text{adsorbed gas}}$ and $Q_{\text{isolate gas}}$ represent the total carried charge of gas molecules after and before adsorption on the surface of Pd-TiO$_2$.

$$Q_{\text{T}} = Q_{\text{adsorbed gas}} - Q_{\text{isolate gas}}$$ \hspace{1cm} (2)

### Results and Discussion

#### The structural parameters of Pd-TiO$_2$, C$_6$H$_7$N and C$_7$H$_9$N

In order to make the geometric structures of Pd-TiO$_2$, C$_6$H$_7$N and C$_7$H$_9$N meet the experimental results, we have obtained the lowest energy structures through DFT methods as shown in Figure 1. On the surface of perfect TiO$_2$ before Pd Doping, there are two types of oxygen atoms, that is O$_{2c}$ (with two coordinate bonds) and O$_{3c}$ (with two coordinate bonds). Similarly, two types of Ti atoms exist on the surface, that is Ti$_{2c}$ (with five coordinate bonds) and Ti$_{3c}$ (with six coordinate bonds). According to study in this work and other researches, the site between two O$_{2c}$ is the most probable site for single Pd atom doping because it reaches the lowest energy and most stable structure. The Pd atom is obviously protrude out of the surface TiO$_2$ with a distance of Pd-oxygen 2.24 Å due to the great radius of Pd atom. The protruding structure of Pd atom acts as an active site to adsorb gas molecules because of its unsaturated bond. The structure of C$_6$H$_7$N is formed by substituting a hydrogen atom with one amidogen on the benzene ring as shown in Figure 1 (A). The bond distances of N-H and N-C are 1.02 Å and 1.40 Å, respectively. And angles of H-N-H and H-N-C are 111.6 degree and 114.5 degree, respectively. For C$_7$H$_9$N molecule, two adjacent hydrogen atoms on benzene ring are replaced by an amidogen and a methyl. The bond distances and angles of amidogen in C$_7$H$_9$N are almost the same with that of C$_6$H$_7$N molecule. The bond distances of C-H and C-C in methyl is 1.11 Å and 1.50 Å, respectively. And the corresponding bond angles are 106.9 degree and 110.9 degree are 1.02 Å and 1.40 Å, respectively.

![Figure 1: The optimized structures: (a) Pd-TiO$_2$, (b) C$_6$H$_7$N and (c) C$_7$H$_9$N. The unit of bond length and angle is Å and degree, respectively.](image)

#### The adsorption structural parameters of C$_6$H$_7$N and C$_7$H$_9$N on the surface Pd-TiO$_2$

In order to ensure the computation accuracy, various approaching manners of C$_6$H$_7$N and C$_7$H$_9$N molecules were considered to find the lowest energy structures. Figure 2 and Table 1 shows the adsorption structural parameters of C$_6$H$_7$N adsorbed Pd-TiO$_2$ (C$_6$H$_7$N/Pd-TiO$_2$) and C$_7$H$_9$N adsorbed Pd-TiO$_2$ (C$_7$H$_9$N/Pd-TiO$_2$).

C$_6$H$_7$N molecule prefers to interact on the surface of Pd-TiO$_2$ through the physisorption between Pd atom and N atom because of their polyvalency property. The interaction distance is 2.20 Å. Due to the activity of Pd atom, the Eads for C$_6$H$_7$N adsorption has reached -1.40 eV. The great $E_{\text{ads}}$ provides the prerequisite to detect C$_6$H$_7$N gas...
in the volatile organic compounds. There are only 0.20 electron transfers from C6H7N molecule to Pd-TiO2. The gas molecule adsorption has no induced the structural change of C6H7N molecule and Pd-TiO2.

C7H8N molecule tends to interact with Pd-TiO2 by hydrogen of the benzene ring. The adsorption distance is 2.83 Å when the adsorption system reaches the lowest energy, which is apparently larger than that of C6H7N/Pd-TiO2. In addition, the E_ads is distinctly less than the adsorption energy of C6H8N/Pd-TiO2. The charge transfer from one C7H8N to Pd-TiO2 is 0.23 e. We conclude that the C7H8N is physically adsorbed on the surface of Pd-TiO2.

Table 1: Adsorption energy (E_ads), charge transfer (Q_f), and the binding distance from the gases to Ni atom.

| System               | Structure | d_ads (Å) | E_ads (eV) | Q_f (e) |
|----------------------|-----------|-----------|------------|--------|
| C7H8N/Pd-TiO2        | -N        | 2.2       | -1.4       | 0.2    |
| C7H8N/Pd-TiO2        | -H        | 2.83      | -0.25      | 0.23   |

The electronic property analysis of adsorption systems

To detect the type and concentration of C6H7N and C7H8N in volatile organic compounds molecules of lung cancer patients, it is necessary to analyse the electronic property analysis of adsorption systems. Basing on the gas detection mechanism of metal oxide resistance-type gas sensor, the Total Density of States (TDOS), Partial Density of States (PDOS), band structure and molecular orbital are calculated by DFT method to analyse the conductivity change of the gas molecules adsorption system.

Figure 3(a) shows the TDOS of adsorption system and PDOS of adsorbed molecules. The Fermi level is located at 0 eV. The TDOS of TiO2 is discontinuous range -2--1 eV, verifying its semiconductor property. When one C6H7N molecule adsorbs on the surface of Pd-TiO2, the TDOS becomes continuous in the entire range of energy. Except the distinct decrease of TDOS range -1--0 eV, TDOS tends to increase at other energy range. Part of the contribution of increased TDOS comes from the PDOS of C6H7N molecule during the adsorption process as show in Figure 3(b). Comparing with the TDOS of C6H7N adsorption system, Though the change of TDOS for C6H7N is similar to that of C6H7N adsorption, but the increment of TDOS range -2--0 eV is obviously larger as shown in Figure 3(c). The PDOS of adsorbed C7H8N molecule also makes great contribution to the increased TDOS C6H8N adsorption system as can be seen in Figure 3(d). According to the increase of TDOS during C6H7N and C7H8N adsorption, we conclude that both of the lung cancer volatile organic compounds increase the conductivity of adsorption system.

Band structure reflects directly the electron filling at different energy level. Figure 4 shows the band structure of Pd-TiO2 and gas adsorbed Pd-TiO2. As can been seen in Figure 4(a), Electronic forbidden band exists in valence band range -2--1 eV, which limit the transition of electron from valence band to conduction band. According to other related study about the band structure of perfect TiO2, the band gap of electronic forbidden band about 2.16 eV from 0--2 eV [30-32]. Therefore, Pd doping has enhanced the conductivity of perfect TiO2 by introducing impurity levels around the Fermi level. For C6H7N and C7H8N adsorption shown in Figure 4(b) and 4(c), The
band structures below -2 eV and above 0 eV are almost the same with that of Pd-TiO$_2$. However, part of band level is distributed from 0~2 eV when C$_6$H$_7$N and C$_7$H$_9$N adsorb on the surface of Pd-TiO$_2$. The impurity levels greatly reduce the transition energy from low level to high level. As a consequence, the conductivity of C$_6$H$_7$N and C$_7$H$_9$N adsorption system is higher than that of Pd-TiO$_2$. This conclusion is consistent with the result of DOS analysis above.

Molecular orbital theory is an effective approximation method to deal with the molecular structure with two or more atoms. Molecular orbital was calculated to further verify the conclusion received by DOS analysis. Figure 5 show the orbital distribution of the Highest Occupied Molecular Orbital (HOMO) and the lowest occupied molecular orbital (LUMO). And Table 2 presents the corresponding value of HOMO, LUMO and energy gap ($E_g$). It is found that the values of $E_g$ for Pd-TiO$_2$ and gas adsorbed Pd-TiO$_2$ are small, signifying their good conductivity.

For Pd-TiO$_2$ shown in Figure 5(a1) and 5(a2) and Table 2, the HOMO mainly locates around Pd atom doping site. And the LUMO mainly locates around the Ti atoms, including a small part on the surface and a main part in the interior of TiO$_2$. Although the distribution location of HOMO and LUMO are not completely overlap, but the small energy gap (1.06 eV) can still ensure the electron transition from HOMO to LUMO.

For C$_6$H$_7$N molecule adsorption shown in Figure 5 (b1) and 5(b2) and Table 2, the value of HOMO and LUMO overall increase with energy gap of 0.05 eV. The HOMO is mainly distributed around Pd and N atoms except a small part around C atoms of C$_6$H$_7$N molecule and Ti atom of TiO$_2$. And the LUMO nearly not occurs on the surface of C$_6$H$_7$N molecule. But it significantly increases around Pd comparing with that before C$_6$H$_7$N adsorption without obvious change on the other site of TiO$_2$. The increased distribution location of HOMO and LUMO will enhance the conductivity of adsorption system.

For C$_7$H$_9$N adsorption shown in Figure 5 (c1) and 5(c2) and Table 2, the value of HOMO and LUMO is almost the same with that before gas adsorption with energy gap of 0.08 eV. Except of the HOMO located on Pd atom, it also largely distributes around C atom of gas molecule. Therefore, the electrons in HOMO can freely transit between Pd-TiO$_2$ and C$_7$H$_9$N molecule. Because of the long interaction distance and weak adsorption energy between Pd-TiO$_2$ and C$_7$H$_9$N molecule, C$_7$H$_9$N adsorption causes little change to the distribution of LUMO on Pd-TiO$_2$, and brings no distribution on gas molecule. Therefore, the conductivity of C$_7$H$_9$N adsorption system increases due to the increase of HOMO distribution.

### Table 2: The HOMO, LUMO energy and HOMO–LUMO energy gap of C$_6$H$_7$N and C$_7$H$_9$N adsorption system.

| System           | $E_{\text{HOMO}}$/eV | $E_{\text{LUMO}}$/eV | $E_g$/eV |
|------------------|----------------------|----------------------|----------|
| Pd-TiO$_2$       | -5.65                | -5.59                | 0.06     |
| C$_6$H$_7$N/Pd-TiO$_2$ | -5.49              | -5.44                | 0.05     |
| C$_7$H$_9$N/Pd-TiO$_2$ | -5.63              | -5.55                | 0.08     |

The first-principles calculation has been applied to analyse the adsorption property of typical lung cancer volatile organic compounds.
CnH7N and CnH7N on Pd-TiO2 surface based on DFT theory. Various
gas adsorptions structures have been calculated to get obtain the most
stable structure shown in this study. Due to the high chemical activity
of Pd atoms, it acts as the active site to adsorb gas molecules. CnH7N
adsorbs by the interaction between Pd atom and N atom of amidogen.
And CnH7N interacts with Pd atom by H atom of benzene ring. The
adsorption energy of CnH7N is distantly less that of CnH7N because of
it larger adsorption distance. And there is little charge transfer in the
adsorption process for both of the gas molecules. The physisorption
between Pd-TiO2 and gas molecules (CnH7N and CnH7N) ensures the
good anti-poisoning ability of gas sensors based on Pd-doped TiO2
material.

According to the analysis of DOS, both of the gas molecules
adsorption increases the DOS near Fermi level. And the band structure
analysis shows that this gas molecules adsorption introduce new
impurity levels around the Fermi level. In addition, gas molecules adsorption makes contribution to increase of the HOMO and LUMO
orbitals on Pd-SWCNTs and molecule-Pd-SWCNTs.

Figure 5: The HOMO and LUMO orbitals on Pd-SWCNTs and
molecule-Pd-SWCNTs

Author Contributions
Qianqian Wan developed the analytical model, and performed
simulations with Materials Studio. Xiaoxing Zhang generated the basic
idea and its application, and supervised the simulation work. All
authors collaborated actively in the writing process.

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