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1. Introduction

Formaldehyde (HCHO) pollution, which is especially mainly concentrated in houses, textiles and food, has been paid more and more attention.^{1,2} This colourless, pungent-smelling gas may do great harm to human health, and is even a carcinogenic risk as concentrations or exposure time increase. In view of its wide use and harmfulness, HCHO detection and removal are required in both residential and industrial environments.^{3,4} In the past few decades, various technologies for gas sensing have been established, including spectrophotometry, chromatography, polarography, and so on.⁵⁻⁹ However, these technologies require sample collection and the instruments are expensive, bulky and sophisticated which limits their application in the real-time monitoring of indoor HCHO. In recent decades, gas sensors based on metal oxide semiconductors, such as TiO2,^{10,11} ZnO,^{12,13} SnO₂,^{14,15} In₂O₃,^{16,17} WO₃,¹⁸⁻²¹ and other complex oxides,^{22,23} have been attractive for the portable real-time



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The on-line detection and treatment of atmospheric formaldehyde (HCHO) at real-time levels, especially in indoor environments, is becoming more and more important. Herein, by first principles calculations, a highly active sub-stoichiometric $WO_{2.9}$ (010) surface for HCHO sensing and treatment has been demonstrated. The exposed one-coordinated terminal O atoms (O_{1c}), two-coordinated bridge O atoms (O_{2c}) and five-coordinated W atoms (W_{5c}) at the surface are found to be active sites for HCHO adsorption. HCHO molecules can anchor on the $WO_{2.9}$ (010) surface through newly formed O_F-W_{5c} and/or $C_F-O_{1c}/O_{2c}/W_{5c}$ bonds, forming 'ridge-like'/'hobbyhorse-like' or slantwise adsorption configurations. The absorbed HCHO molecules may exchange electrons with the $WO_{2.9}$ (010) surface and change the conductivity of the surface, which is the working mechanism of $WO_{2.9}$ based sensors. Furthermore, Cl-NEB results suggest that the absorbed HCHO molecules tend to dissociate under moderate excitation (for example, solar visible light) at room temperature due to the minimum energy barrier of only 0.54 eV. The HCHO dissociation results in an H adatom bond to a surface O_{1c} atom and a formate or formyl group chemisorbed to the surface with elongated O_F-W_{5c} and C_F-W_{5c} bonds, which means that O_F-W_{5c} and C_F-W_{5c} bonds are active and prone to breaking. These results demonstrate the potential of $WO_{2.9}$ in HCHO sensing and elimination.

measurement of toxic gases due to their high sensitivities, fast responses and low cost.

As an important oxide semiconductor, WO₃ has ignited intensive interest for application in gas sensors. However, both experimental and theoretical research into the gas sensitivity of WO_3 mainly concern CO, H_2S , NO_x , and H_2 , as well as some organic gases,19-21,24 while WO3 based HCHO sensors have been occasionally studied only in the past several years. In 2012, Deng et al. reported mesoporous WO₃ sensors with enhanced HCHO-sensing properties under visible-light irradiation, which operated at room temperature.25 In the past year, an Fe-doped WO₃ based sensor for HCHO (50 ppm) at an operating temperature of 225 °C has been investigated by Upadhyay et al.26 It is noteworthy that both works have made efforts to enhance the HCHO-sensing properties through either morphology modifications or metal atoms doped in WO₃. Thus it can be seen that it's very important to modify the pristine oxide semiconductor to enhance its sensing performance.

To tune WO₃ into a more active sensing material, many other approaches have been employed, such as the deposition of metal nanoparticles as catalytic additives on the WO₃ surface¹⁹ and the synthesis of WO₃ with various dimensionalities and morphologies.^{20,24} Recently, tungsten oxide with deficient oxygen (WO_{3-x}, 0 < x < 1) content has attracted much attention because of its unique structural and electronic properties. Shpak *et al.* have demonstrated that sub-stoichiometric WO_{2.9} and WO_{2.72} exhibit better H₂-sensing performance compared



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with stoichiometric WO3.27 Hu et al. reported that a nanocomposite of n-WO_{3-x}/n-porous silicon showed enhanced NO₂sensing properties, and that the large amount of oxygen vacancies in n-WO_{3-x} is one of the main factors in the performance improvement.²⁸ It's well known that when target gases come in contact with sensors, the absorption of gas on the semiconductor and the electron exchange between them will change the conductivity of the sensor. This simple working mechanism indicates that the quality of sensors is determined by the interaction between the target gases and the sensing materials. Therefore, it is very meaningful to study the absorption behaviour of various toxic gases towards metal oxide semiconductors for the development of high performance sensors. Recently, Li et al. reported a facile thermal treatment to modify the local structure of WO₃ at an atomic level, to activate the stoichiometric tungsten oxide into sub-stoichiometric WO_{2.9}. They found that the catalytic activity for hydrogen evolution in acidic water was effectively enhanced due to the improved H adsorption ability at the five-coordinated W atom in the local defect region of the WO_{2,9} (010) surface.²⁹ What's more, Wang et al. have reported that WO_{2.9} shows similar absorption edges at around 480 nm, which is consistent with the WO3 band gap of 2.6 eV (which could theoretically utilize 12% of solar light) and exhibits almost the same position of valence band maximum as that of WO₃.³⁰ So we anticipate that the local defect region of such a defective $WO_{2,9}(010)$ surface might be suitable for effective HCHO absorption and that WO_{2.9} is an alternative material for HCHO sensing and treatment under visible-light irradiation.

In this work, we have studied HCHO absorption behavior towards a WO_{2.9} (010) surface using first principles calculations for the first time. Total energy calculation results indicate that WO_{2.9} (010) exhibits excellent absorption properties for HCHO molecules due to the activity of exposed atoms at the surface. HCHO molecules can absorb on the WO_{2.9} (010) surface through newly formed O_F -W_{5c} and/or C_F -O_{1c}/O_{2c}/W_{5c} bonds, forming 'ridge-like'/'hobbyhorse-like' or slantwise adsorption configurations. As expected, the adsorption energies of HCHO molecules in the defect region of the WO_{2.9} (010) surface are higher than those out of the defect region. What's more, the absorbed HCHO molecules dissociate across an energy barrier of 0.54 to 1.94 eV under solar visible light or other moderate excitation, resulting in a H adatom bond to a surface O_{1c} atom and a formate or formyl group chemisorbed to the surface, with elongated O_F-W_{5c} and/or C_F-W_{5c} bonds which tend to break under moderate irradiation, even at room temperature. The findings in this work may hold promise for the development of HCHO sensing and treatment methods.

2. Computational method

Our theoretical calculations are based on DFT within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation³¹ and the projected augmented wave (PAW) method^{32,33} as implemented in the Vienna ab initio simulation package (VASP). To reach the convergence criteria for both the energy and forces, special K-point sampling with a k-point separation of 0.03 \AA^{-1} is applied for the Brillouin-zone integration and the cutoff energy for the plane wave basis set is 600 eV. The ground state geometries of the bulk and surfaces are obtained with all the atomic positions relaxed until their residual forces are less than 0.05 eV $Å^{-1}$. The calculated lattice parameters for the bulk monoclinic WO_{2.9} (a = 12.20 Å, b = 3.82 Å, c = 23.87 Å, and $\beta = 94.51^{\circ}$) are a little greater than the experimental values (a = 12.05 Å, b =3.77 Å, c = 23.59 Å, and $\beta = 94.72^{\circ}$),²⁹ which suggests the PBE method may provide 98% accuracy in describing the lattice structures. The surface models are constructed from the optimized bulk unit cell and a vacuum thickness of 15 Å is adopted in building the periodic slab models.

For the WO_{2.9} (010) surface, a slab consisting of seven atomic monolayers is constructed and the geometric structure is shown in Fig. 1. As Li *et al.* have reported, half of the surface oxygen atoms are transferred from the top to the bottom layer to cancel the dipole effect, similar to the ($\sqrt{2} \times \sqrt{2}$) *R*45° reconstruction of the WO₃ (001) surface.²⁹ For convenience, the characters T_n, B_n (B'_n), and W_n indicate the exposed one-coordinated terminal O



Fig. 1 Optimized structures of a clean $WO_{2.9}$ (010) surface: (a) side view, and (b) top view. Red and cyan balls represent O and W atoms, respectively. Just to be clear, the surface one-coordinated terminal O atoms are indicated by pink balls. The $WO_{2.9}$ (010) surface is artificially divided into a defect region, which is covered by the light gray shaded area, and the region out of the defect region.

Before adsorption, the isolated HCHO molecule is simulated in a large cubic cell of 15 Å in length, and the O, C, and H atoms of HCHO are denoted as O_F , C_F , H_F here. HCHO adsorption is investigated by placing two HCHO molecules symmetrically on both sides of the slab to eliminate the dipole effect. For all the absorption configurations, the atomic positions are fully relaxed. The adsorption energies are calculated following the equation $E_{ads} = E_{HCHO} + E_{surface} - E_{HCHO/surface}$, where $E_{HCHO/surface}$, E_{HCHO} , and $E_{surface}$ are the total energies of the WO_{2.9} (010) surface with the adsorbed HCHO molecule, the isolated HCHO molecule, and the $WO_{2,9}$ (010) surface without an adsorbent, respectively. The HCHO adsorption at various coverages is investigated to clarify the high absorption performance of HCHO on $WO_{2.9}$ (010) surfaces. Density of states (DOS), partial density of states (PDOS) and difference charge density are obtained at the optimized geometry. Moreover, we have investigated the dissociative pathway for absorbed HCHO molecules using the climbing image nudged elastic band (Cl-NEB) method for finding saddle points and minimum energy paths between known reactants and products^{34,35} and demonstrated the possibility of the treatment of HCHO using a WO_{2.9} (010) surface.

Results and discussion 3.

Molecule adsorption of HCHO on a WO_{2.9} (010) surface 3.1

A number of molecule absorption configurations for HCHO on a $WO_{2.9}(010)$ surface have been considered to explore the stable absorption states. According to calculations, physically adsorbed HCHO molecules tend to deviate from the surface or transform into chemically absorbed HCHO, because of the small physical adsorption energies (<26 meV). Contrarily, HCHO molecules prefer to anchor on the WO_{2.9} (010) surface through chemisorption with larger adsorption energies. Herein we will discuss the chemisorption states of HCHO in detail.

Through total energy calculations, the most stable molecule absorption configurations (type I) for HCHO on the $WO_{2,9}$ (010) surface are depicted in Fig. 2(a)-(c). The O_F atom binds to a surface W_{5c} atom and simultaneously the C_F atom binds to a surface O1c atom, forming a 'ridge-like' closed ring. The bond lengths of the newly formed OF-W5c bond and CF-O1c bond are about 1.90 Å and 1.41 Å, respectively. Moreover, the C_F-H_F bond of HCHO is slightly shortened to 1.10 Å (0.02 Å shorter) and the $C_F - O_F$ bond of HCHO is lengthened to 1.42 Å, 0.21 Å longer than that of an isolated HCHO molecule. As expected, the absorption energies of HCHO absorbed in the defect region are 2.18 eV (Fig. 2(b)) and 1.81 eV (Fig. 2(c)), higher than that out of the defect region (1.59 eV, Fig. 2(a)). For comparison, the absorption energies of different configurations are summarized in Table 1.

In the second stable molecule absorption configuration shown in Fig. 2(d) (type II), HCHO interacts with the WO_{2.9} (010) surface through both the O_F and C_F atoms bonding to the surface W_{5c} atoms, also in the form of a 'ridge-like' closed ring. The $C_F - O_F$ and $C_F - H_F$ bond lengths of the absorbed HCHO of this type are similar to those of type I. The bond lengths of O_F-W_{5c} and C_F-W_{5c} are 1.91 Å and 2.27 Å, respectively, and the absorption energy is 1.38 eV.

Fig. 2 Side and top views of the molecule absorption configurations for HCHO molecules on a WO_{2.9} (010) surface: (a)–(c) represent the most stable 'ridge-like' states, denoted as type I; (d) is the second stable state, denoted as type II; (e)–(g) indicate 'hobbyhorse-like' absorption states, denoted as type III; and (h) and (i) show slantwise absorption, denoted as type IV. Red, cyan, gray and white balls represent lattice O atoms, W atoms, C atoms and H atoms, respectively. Pink balls indicate surface one-coordinated terminal O atoms.





Table 1 The absorption energies of different molecule adsorption configurations of $W_n - T_{n'} W_n - B_n (W_n - B'_n)$, and W_n , where W_n denotes the surface exposed W_{5c} atom which bonds to an O_F atom, and T_n/B_n (B'_n) represents a surface O_{1c}/O_{2c} atom which bonds to a C_F atom. $W_n - T_n$ and $W_n - B_n (W_n - B'_n)$ indicate absorption configurations with two newly formed bonds of $C_F - O_{1c}/O_{2c}$ (type I/II) and $O_F - W_{5c}$ (type III). W_n expresses absorption configurations with only one newly formed bond of $O_F - W_{5c}$ (type IV)

Configuration	$E_{\rm ads}$ (eV)	Configuration	$E_{\rm ads} ({\rm eV})$
W T	1 50	W D	0.00
W ₁ -1 ₁	1.50	W ₁ -B ₁	0.96
$W_1 - T_2$	1.54	W_1-B_2	0.88
W_1-T_3	1.59	W_1-B_3	0.96
W_1-T_4	1.49	W_1-B_4	0.86
W_2-T_1	1.74	W_2 -B'1	0.96
W_2-T_2	1.76	$W_2-B'_2$	0.58
W_2-T_5	1.52	W_2-B_5	0.70
W_2-T_6	2.18	W_2-B_6	1.03
W3-T6	1.74	$W_3-B'_6$	0.95
W_3-T_7	1.72	W_3-B_7	0.93
W ₃ -T ₈	1.68	W_3-B_8	0.87
W3-T9	1.81	W ₃ -B ₉	0.89
$W_4 - T_{10}$	1.50	$W_5 - W_6$	1.38
W_1	1.04	W_5	1.01

HCHO can also chemisorb to a WO_{2.9} (010) surface similarly to the most stable absorption configuration, expect that the C_F atom binds to a surface O_{2c} atom rather than an O_{1c} atom, while the O_F atom still binds to an exposed W_{5c} atom. These absorption configurations are also closed rings and look like a 'hobby-horse' (type III). Though the absorption energies of these configurations are below 1.0 eV, these absorption states are stable, with bond lengths of 1.93 Å and 1.47 Å for the newly formed O_F - W_{5c} and C_F - O_{2c} bonds, respectively. The structures and bond lengths of the absorbed HCHO molecules have similar changes to those of type I.

What's more, HCHO absorbed to the WO_{2.9} (010) surface solely through the O_F atom bonding to a surface W_{5c} atom, forming a slantwise absorption (type IV) relative to the surface, with an absorption energy of about 1.00 eV. The bond length of the newly formed O_F–W_{5c} is about 2.20 Å. In this kind of absorption type, the C_F–O_F bond of HCHO is 1.23 Å, close to that of an isolated HCHO molecule, indicating that the structural change in the absorbed HCHO molecule is very small. Absorption configurations with only one newly formed chemical bond between the C_F atom and surface W_{5c} atom have also been studied. However, the atomic relaxation can't converge to a local minimum, indicating the impossibility of the absorption state.

It's worth noting that the type I and III adsorption configurations involve bonding between C_F and the lattice O (O_{1c} or O_{2c}) on WO_{2.9} (010), and reaction barriers could exist in such processes owing to electronic repulsion. Comparing the absorption structures of the four types, we have found that type I and III adsorption configurations may be transformed from type IV. Therefore, the barriers and corresponding transition states of type I and III adsorption configurations are studied and presented in Fig. S3,† in which the initial structure is W₁ in type IV and the final structures are W₁–T₃ in type I and W₁–B₃ in type III, respectively. Cl-NEB results reveal that the reaction barriers for the transformation from W_1 to W_1 -T₃ and W_1 -B₃ are 0.52 eV and 0.37 eV, respectively, which ensures the possibility of type I and III adsorption configurations.

To further investigate the absorption properties of HCHO on a WO_{2.9} (010) surface, we have also investigated the coverage dependent HCHO absorption on a WO_{2.9} (010) surface. The absorption energy variation with coverage is nearly linear, as shown in Fig. S1.[†] The absorption energy for full monolayer coverage is about 1.30 eV, through an extrapolation approximation, implying that the WO_{2.9} (010) surface exhibits excellent HCHO absorption properties.

3.2 Electronic properties of the $WO_{2.9}$ (010) surface with HCHO absorption

The electric structure of the WO_{2.9} (010) surface has been studied through a further analysis of total and partial density of states. As seen from the TDOS and PDOS of clean $WO_{2,9}$ (010) shown in Fig. S2,[†] the top of the valence band mainly originates from O atoms, while the bottom of the conduction band is mainly from W atoms. What's more, the PDOS of W atoms shows that the Fermi level of the WO_{2.9} (010) surface is higher than the bottom of the conduction band, indicating evident metallic properties. Further partial charge analysis reveals that the band appearing across the Fermi level mainly originates from W_{5c} atoms, which favours electron transfer from W_{5c} to O_F and bonding between W_{5c} and O_F. Fig. 3 presents the TDOS and some atomic PDOS for a HCHO absorbed WO2.9 (010) surface with the stable configurations presented in Fig. 2. To facilitate a comparison, the TDOS of a clean $WO_{2.9}$ (010) surface is always shown and the Fermi level of the WO2.9 (010) surface is assigned at 0 eV. Obviously, new electronic states occur at around -12 eV and -21 eV after HCHO absorption for type I, III and IV, while new electronic states arise only at around -12 eV for absorption type II. The PDOS for the C_F/O_F atom and for the corresponding O_{1c}/W_{5c} surface atom which is bound to the C_F/O_F atom are considered. The PDOS for the C_F/O_F atom is broadly dispersed compared to that for gas-phase HCHO (see Fig. S1[†]) and an overlap between C_F and O_{1c} atoms and between O_F and W_{5c} atoms can be clearly seen. These PDOS results indicate the obvious charge redistribution and newly formed covalent bonds for $C_F - O_{1c}$ and $O_F - W_{5c}$.

To understand the local charge transfer between the most stable adsorbed HCHO molecules and the WO_{2.9} (010) surface, which is the primary mechanism for HCHO sensing properties, we have investigated the charge density difference originating from adsorption, presented in Fig. 4, in which the blue wireframes denote a loss of electrons while yellow wireframes denote a gain of electrons. For absorption types I and III, there is obvious charge transfer from the surface W_{5c} atom to the O_F atom and from the C_F atom to the surface O_{1c} atom, as shown in Fig. 4(a)–(c) and (e)–(g), which agrees well with the PDOS results presented in Fig. 3(a) and (c), indicating the strong binding of the HCHO molecule to the defect sites on the WO_{2.9} (010) surface. As seen from Fig. 4(d), charge transfer mainly occurs between the O_F atom and surface W_{5c} atom for absorption type



Fig. 3 DOS and PDOS for a HCHO absorbed WO_{2.9} (010) surface of (a) type I, (b) type II, (c) type III, and (d) type IV. The black curves present the TDOS for a WO_{2.9} (010) surface and the TDOS of the clean surface is always plotted to facilitate comparison. The blue curves denote the DOS for WO_{2.9} (010) surfaces with absorbed HCHO molecules. Red curves are PDOS for the C_F atom of HCHO molecules and the olive curves are PDOS of O_{1c} atoms (bound to the C_F atom of HCHO) of the WO_{2.9} (010) surface. Dark yellow curves represent PDOS for the O_F atom of HCHO molecules and magenta curves represent PDOS of the W_{5c} atoms (bound to the O_F atom of HCHO) of the WO_{2.9} (010) surface. The Fermi level of the WO_{2.9} (010) surface is assigned at 0 eV.

II, while the amount of charge transfer between the C_F atom and surface W_{5c} atom is small, in accordance with the bond lengths of O- W_{5c} and C- W_{5c} and the PDOS results shown in Fig. 3(b). Obviously, for the slantwise absorption state of type IV, the only charge transfer occurs between the O_F atom and the surface W_{5c} atom, while the impact on the charge distribution of C_F is tiny and the peaks in the PDOS for C_F in absorption of type III are relatively sharp, as shown in Fig. 3(d). Moreover, for these slantwise absorption configurations, there is a hydrogen bond between the H_F atom and surface O_{1c} atom, besides the charge transfer between the O_F atom and surface W_{5c} atom, which can be seen from Fig. 4(h) and (i).

3.3 Dissociative adsorption of HCHO on the WO_{2.9} (010) surface

To investigate the possibility of HCHO dissociation on the $WO_{2.9}$ (010) surface, we first start with the stable molecule absorption configuration shown in Fig. 2, which means the



Fig. 4 The isosurface of the difference in charge density with an isovalue of 0.003 Å^{-3} ; the blue (yellow) wireframes denote a loss (gain) of electrons. (a)–(i) correspond to the isosurface of structures presented in Fig. 2(a)–(i), respectively. Red, cyan, gray and white balls represent lattice O atoms, W atoms, C atoms and H atoms, respectively. Pink balls indicate surface one-coordinated terminal O atoms.

initial states are those HCHO molecules absorbed on a $WO_{2.9}$ (010) surface of type I, II, III and IV, while the final states are the relaxed structures of a dissociative adsorption configuration, with one formate/formyl group and one H adatom absorbed to the surface, which result from the rupture of the C–H bond in the absorbed HCHO molecule and then the lively H atom binds to an adjacent O_{1c} atom. And the transition states are determined as those structures of saddle points obtained using the Cl-NEB method.

As presented in Fig. 5(a), in the dissociation reaction, the C-H bond scission is accompanied by a rotation of the other C-H bond toward the surface normal. The minimum energy path for the dehydrogenation reaction of HCHO determined by the Cl-NEB method is also shown with an overall reaction barrier of 1.12 eV, and the energy change between the initial and final states is -0.48 eV (an exothermic process). The bond lengths of C-O, the C-H bond in the HCHO structure and the corresponding O-W bond lengths of the transition state (TS) are quite close to those of the initial state (IS), meaning that the TS is more reactant-like than product-like. After the dehydrogenation reaction, the bond lengths of the C-O bonds in the HCO₂ structure are shortened to 1.27 Å and 1.28 Å, while the bond lengths of the O-W bonds between HCO2 and the surface are enlarged to 2.12 Å and 2.16 Å, indicating that the formate can deviate from the surface under moderate conditions.

Fig. 5(b) presents the reaction pathway for the dehydrogenation of absorbed HCHO molecules of type II. Similarly, the C–H bond scission is accompanied by a rotation of the other C–H bond, with the bond length almost unchanged. The dehydrogenation reaction needs to cross two transition states and the highest barrier is only 0.54 eV, which can be easily surmounted. What's more, the energy change between the initial and final states is 0.06 eV, indicating a weakly endothermic process. In the FS, the bond length of C_F – W_{5c} shows almost no change, while the bond length of the O_F – W_{5c} bond is lengthened to 2.19 Å (0.28 Å longer). The fact that there are large bond lengths for O_F – W_{5c} and C_F – W_{5c} between the formyl group (HCO) and the surface allows us to propose an assumption that



Fig. 5 The minimum energy path for the dehydrogenation reaction of absorbed HCHO molecules (a) of type I; (b) of type II; (c) of type II; and (d) of type IV. For all dehydrogenation reactions, the C–H bond scission is accompanied by a rotation of the other C–H bond, with the bond length almost unchanged. The red, cyan, gray and white balls represent lattice O atoms, W atoms, C atoms and H atoms, respectively. Pink balls indicate surface one-coordinated terminal O atoms.

the formyl group is highly active and prone to oxidation, even at room temperature under solar visible irradiation. The bond lengths of the corresponding TS2 are quite close to those of the FS, suggesting that the TS is more product-like than reactantlike.

The dehydrogenation pathway for the HCHO structure in a 'hobbyhorse' configuration of type III is shown in Fig. 5(c). The dehydrogenation reaction needs to cross three transition states with a highest barrier of 1.94 eV, and the energy change between the initial and final states is 0.03 eV (a weakly endothermic process). The bond lengths of the C–O bonds in the HCO₂ structure are shortened to 1.25 Å and 1.34 Å, and the length of the corresponding O–W bond between HCO₂ and the surface is enlarged to 2.17 Å, which means that the O–W bond can be broken easily leaving a chemisorbed formyl group on the surface. The bond lengths of the corresponding transition state (TS) are quite close to those of the final state (FS), suggesting that the TS is more product-like than reactant-like.

Interestingly, by analysing the reaction pathway for the dehydrogenation of absorbed HCHO molecules of type IV, we have found that the molecule absorption of HCHO of type IV tends to turn into a more stable absorption configuration, just like type II, across an energy barrier of only 0.19 eV, which can be seen from the transform pathway presented in Fig. S4.† The simulated minimum energy path indicates the absorption

configuration of type II is more stable, 0.40 eV lower per HCHO absorbed on the $WO_{2.9}$ (010) surface than for the absorption configuration of type IV. Therefore, we study the dehydrogenation reaction of absorbed HCHO molecules of type IV starting with a configuration of type II. The reaction pathway is shown in Fig. 5(d) and the overall reaction barrier is 0.97 eV. The total energy change, TS and FS are similar to those of Fig. 5(b) and the TS is also more product-like than reactant-like.

In consideration of the energy barrier of 0.54 to 1.94 eV for the four types of dissociation reaction and the band gaps and edges of WO_{2.9} which are appropriate for HCHO sensing,^{25,30} HCHO dissociation can occur under moderate excitation at room temperature, such as under visible light irradiation. The adsorption and dissociation properties of HCHO on a WO_{2.9} (010) surface indicate that sub-stoichiometric WO_{2.9} may find potential application in HCHO sensing and elimination at room temperature.

4. Conclusions

We have systematically investigated the HCHO absorption performance on a sub-stoichiometric $WO_{2.9}$ (010) surface using first principles calculations. The calculated results suggest that exposed O_{1c} , O_{2c} and W_{5c} atoms at the surface are active sites for HCHO adsorption, and HCHO molecules can fasten on the surface mainly in four types through newly formed O_F-W_{5c} and/ or $C_F-O_{1c}/O_{2c}/W_{5c}$ bonds. HCHO molecules chemisorbed to the $WO_{2.9}$ (010) surface are inclined to dehydrogenate across an energy barrier of 0.54 to 1.94 eV, leaving formate or formyl groups and H adatoms absorbed on the surface. The larger bond lengths between the formate/formyl group and the surface mean that the activity of the formate/formyl group may deviate from the surface under moderate irradiation, resulting in nontoxic CO₂ or HCOOH finally. These results indicate that a substoichiometric $WO_{2.9}$ (010) surface is appropriate for HCHO sensing and elimination at room temperature under moderate conditions, for example, visible-light irradiation, electrochemical excitation, and so on.

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References

- 1 Y. I. Korpan, M. V. Gonchar, A. A. Sibirny, C. Martelet, A. V. Ela rskaya, T. D. Gibson and A. P. Soldatkin, *Biosens. Bioelectron.*, 2000, **15**, 77–83.
- 2 J.-Y. An, S. Kim, H.-J. Kim and J. Seo, *Build. Environ.*, 2010, 45, 1826–1833.
- 3 G. McGwin Jr, J. Lienert and J. I. Kennedy Jr, *Environ. Health Perspect.*, 2010, **118**, 313.
- 4 M. Cordiner, A. Remijan, J. Boissier, S. Milam, M. Mumma, S. Charnley, L. Paganini, G. Villanueva, D. Bockelée-Morvan, Y.-J. Kuan, *et al.*, *Astrophys. Lett.*, 2014, **792**, L2.
- 5 P. Zhou, D. Zhou, L. Tao, Y. Zhu, W. Xu, S. Xu, S. Cui, L. Xu and H. Song, *Light: Sci. Appl.*, 2014, 3, e209.
- 6 N. Li, A. Tittl, S. Yue, H. Giessen, C. Song, B. Ding and N. Liu, *Light: Sci. Appl.*, 2014, **3**, e226.
- 7 T. Allsop, R. Arif, R. Neal, K. Kalli, V. Kundrát, A. Rozhin, P. Culverhouse and D. J. Webb, *Light: Sci. Appl.*, 2016, 5, e16036.
- 8 J. M. Lorrain, C. R. Fortune and B. Dellinger, *Anal. Chem.*, 1981, 53, 1302–1305.
- 9 J. C. Septon and J. C. Ku, *Am. Ind. Hyg. Assoc. J.*, 1982, **43**, 845–852.
- 10 S. Lin, D. Li, J. Wu, X. Li and S. Akbar, *Sens. Actuators, B*, 2011, **156**, 505–509.
- 11 P. Zhou, X. Zhu, J. Yu and W. Xiao, ACS Appl. Mater. Interfaces, 2013, 5, 8165–8172.
- 12 L. Zhang, J. Zhao, H. Lu, L. Gong, L. Li, J. Zheng, H. Li and Z. Zhu, Sens. Actuators, B, 2011, 160, 364–370.

- 13 Q. Huang, D. Zeng, H. Li and C. Xie, *Nanoscale*, 2012, 4, 5651–5658.
- 14 Y. Zhang, X. He, J. Li, Z. Miao and F. Huang, *Sens. Actuators, B*, 2008, **132**, 67–73.
- 15 T. Van Dang, N. Duc Hoa, N. Van Duy and N. Van Hieu, ACS Appl. Mater. Interfaces, 2016, **8**, 4828–4837.
- 16 S. Wang, B. Xiao, T. Yang, P. Wang, C. Xiao, Z. Li, R. Zhao and M. Zhang, J. Mater. Chem. A, 2014, 2, 6598–6604.
- 17 J. Cao, H. Dou, H. Zhang, H. Mei, S. Liu, T. Fei, R. Wang, L. Wang and T. Zhang, Sens. Actuators, B, 2014, 198, 180–187.
- 18 J. Kukkola, J. Mäklin, N. Halonen, T. Kyllönen, G. Tóth, M. Szabó, A. Shchukarev, J.-P. Mikkola, H. Jantunen and K. Kordás, Sens. Actuators, B, 2011, 153, 293–300.
- 19 Y. Wang, X. Cui, Q. Yang, J. Liu, Y. Gao, P. Sun and G. Lu, *Sens. Actuators, B*, 2016, **225**, 544–552.
- 20 Z. Xie, Y. Zhu, J. Xu, H. Huang, D. Chen and G. Shen, *CrystEngComm*, 2011, **13**, 6393–6398.
- 21 H. Long, W. Zeng and H. Zhang, J. Mater. Sci., 2015, 26, 4698-4707.
- 22 M. K. Verma and V. Gupta, *Sens. Actuators, B*, 2012, **166**, 378–385.
- 23 X. Wang, W. Wang, H. Li, C. Fu, Y. Ke and S. He, Sens. Actuators, B, 2012, 169, 10-16.
- 24 H. G. Moon, S. D. Han, M.-G. Kang, W.-S. Jung, B. Kwon, C. Kim, T. Lee, S. Lee, S.-H. Baek, J.-S. Kim, et al., Sens. Actuators, B, 2016, 229, 92–99.
- 25 L. Deng, X. Ding, D. Zeng, S. Tian, H. Li and C. Xie, *Sens. Actuators, B*, 2012, **163**, 260–266.
- 26 S. Upadhyay and P. Sahay, Nanomaterials, 2015, 10, 1550113.
- 27 A. Shpak, A. Korduban, M. Medvedskij and V. Kandyba, *J. Electron Spectrosc.*, 2007, **156**, 172–175.
- 28 M. Li, M. Hu, D. Jia, S. Ma and W. Yan, Sens. Actuators, B, 2013, 186, 140–147.
- 29 Y. H. Li, P. F. Liu, L. F. Pan, H. F. Wang, Z. Z. Yang, L. R. Zheng, P. Hu, H. J. Zhao, L. Gu and H. G. Yang, *Nat. Commun.*, 2015, 6, 8064.
- 30 G. Wang, Y. Ling, H. Wang, X. Yang, C. Wang, J. Z. Zhang and Y. Li, *Energy Environ. Sci.*, 2012, 5, 6180–6187.
- 31 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865.
- 32 J. Furthmüller, J. Hafner and G. Kresse, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 15606.
- 33 G. Kresse and D. Joubert, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 1758.
- 34 G. Henkelman, B. P. Uberuaga and H. Jónsson, J. Chem. Phys., 2000, 113, 9901–9904.
- 35 G. Henkelman and H. Jónsson, J. Chem. Phys., 2000, 113, 9978–9985.