

First-Principles Study on Hexagonal WO₃ for HCHO Gas Sensing Application

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Abstract The adsorption energy, electronic structure, density of states, and electron population for adsorption of HCHO on the hexagonal WO₃ (h-WO₃) (001) surfaces were investigated by density functional theory calculations. The adsorption energy of HCHO molecule on W and O sites of WO-terminated h-WO₃ (001) surface was -0.309 and -0.432 eV compared with the value at -1.936 eV for HCHO molecule on O-terminated h-WO₃ (001) surface. According to the calculated results, the adsorption of HCHO on h-WO₃ (001) surface was spontaneous with physical adsorption on WO-terminated h-WO₃ (001) surface and chemisorption on O-terminated h-WO₃ (001) surface. The charge transfer from adsorbed HCHO molecule to WO₃ (001) surface was confirmed by the Mulliken population analysis, which suggested the potential application of h-WO₃ for HCHO gas detection.

KEY WORDS: Semiconductors; Surfaces; Crystal structure; Electronic structure

1 Introduction

Monitoring and detection of toxic gas are attracting more and more attention of researchers because it is closely connected with the public health and safety. Typically, formaldehyde (HCHO) gas is a colorless, strong-smelling, and well-known carcinogen often coming from building

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National Engineering Laboratory for Textile Fiber Materials and Processing Technology (Zhejiang), Hangzhou 310018, China materials, interior decoration materials, wood furniture, and so on [1, 2]. Usually, HCHO gas can harm people's health at low levels, including irritating human eyes and nose, or causing headache [3]. Thus, it is very necessary to detect HCHO accurately.

Fortunately, nanostructure metal oxide semiconductors have shown the advantages of low cost, high sensitivity, fast response, quick recovery, and excellent stability in detecting gas pollutants [4–10]. As an important semiconductor material, WO₃ is widely used to detect various organic or inorganic gases. Qin et al. [11] found that monoclinic WO₃ (m-WO₃) exhibited excellent NO₂ sensing properties. However, it was dissatisfactory to detect other gases due to their inherent space structure [12–16]. Recently, several studies have shown that hexagonal WO₃ (h-WO₃) had considerable gas sensitivity on a good many of different gases (such as H₂S, NH₃, NO₂, and CO) [14, 17–19]. The difference of gas sensitivity on m-WO₃ and h-WO₃ attracted increasing attention.

Generally, the sensing properties of metal oxide gas sensors are evaluated by monitoring the variation of the electrical conductivity [11, 20]. And the electrical conductivity of metal oxide is closely related to their electronic structure. However, not all the gas molecule adsorbed on the surface of metal oxide would lead to an obvious variation in resistance. Thus, it is very important to understand electronic structure of metal oxide before and after gas adsorption theoretically. Tian et al. [21] investigated the effect of CO gas adsorbed on h-WO₃ (001) surface by density functional theory, in which they analyzed the variation of electronic structure of h-WO3 (001) surface and Mulliken population of CO before and after adsorption and predicted a high sensitivity of h-WO₃ to CO gas.

Determining the sensitivity of h-WO₃ to HCHO gas was quite necessary. Herein, the band structure, the density of the states, the adsorption energy, and Mulliken population of HCHO-adsorbed h-WO₃ (001) surface were investigated scientifically by first-principles theory. The calculated results indicated the adsorption of HCHO molecule was spontaneous. Moreover, it had an obvious variation in electronic structure of h-WO₃ (001) surface after the adsorption of HCHO and led to the charges transfer between adsorbed HCHO molecule and h-WO₃ (001) surface, which implied the conductivity of the surface of h-WO₃ (001) would be changed before and after the adsorption of HCHO. It indicated the h-WO₃-based material is highly sensitive in detecting HCHO gas.

2 Calculation and Modeling

In this paper, all the structure optimizations, the band structures, the density of the states, and the energy calculations were carried out by using the Cambridge Serial Total Energy Package (CASTEP) codes in Materials Studio [12, 22]. The ultrasoft pseudo-potentials and generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional were adopted. The cutoff energy for plane-wave was set to be 380 eV, and the minimization algorithm was chosen to be the Broyden–Fletcher–Goldfarb–Shanno (BFGS) scheme. The energy, force, stress, and displacement convergence criteria for structure optimization and energy calculation were set at 1.0×10^{-5} eV/atom, 0.03 eV/Å, 0.05 GPa, and 0.001 Å, respectively. All the calculations in this paper

were fully converged. The computational models for h-WO₃ (001) surface were constructed by a periodic (2×1) slab model with a thickness of three layers. A vacuum of 15 Å was added to the slab in order to avoid the interactions of adjacent slab model. The Monkhorst-Pack k-point sampling was set as $3 \times 3 \times 6$ for the bulk WO₃, $1 \times 1 \times 1$ for the clean WO₃ (001) surface and adsorption (001) surfaces. All geometrical structures were fully optimized before adsorption, and all the atoms including WO₃ and HCHO were relaxed when HCHO adsorbed on the h-WO₃ (001) surface. All calculations were performed in the reciprocal space. For calculations of isolated HCHO molecule, a box of $10 \times 10 \times 10 \text{ Å}^3$ was used. According to previous studies, the gas adsorption was probably taken place on W and O sites of WO₃ (001) surface [21]. Thus, the adsorption of HCHO molecule on these two sites will be studied. The adsorption energy E_{ads} was calculated by employing the following equation:

$$E_{\rm ads} = E_{\rm HCHO/surface} - (E_{\rm HCHO} + E_{\rm surface})$$

where $E_{\text{HCHO/surface}}$ is the total energy of the surface with HCHO adsorption, E_{HCHO} is the energy of an isolated HCHO molecule and E_{surface} is the energy of clean (001) surface slab [21, 23, 24]. Undoubtedly, a negative value of E_{ads} indicates a favorable adsorption system.

3 Results and Discussion

The lattice parameters with a = b = 0.74169 nm, c = 0.38104 nm are obtained after geometry optimization for h-WO₃ crystal structure. These results are in good agreement with previous theoretical and experimental values (Table 1), which indicated the reliability of our calculation method in this paper [25–27]. Figure 1a shows the band structure of bulk h-WO₃. The conduction band minimum (CBM) and valence band maximum (VBM) located at the different *k*-points (G and H) indicate h-WO₃ is an indirect band gap semiconductor. The calculated band gap is ca. 2.209 eV between CBM and VBM, which is smaller than the experimental value of 3.48 eV due to the shortcoming of the theory frame of density functional theory (DFT)–GGA to underestimate band gaps [28]. The

Table 1 Calculated and experimental values of the lattice parameters of h-WO3

Method	$a \ (10^{-1} \text{ nm})$	$c \ (10^{-1} \text{ nm})$	c/a	и	References
DFT-GGA-PBE	7.4169	3.8104	0.5137	0.5000	This work
DFT-GGA-PBE	7.410	3.808	0.514	0.500	[25]
DFT-GGA	7.410	3.814	0.515		[26]
Experimental	7.298	3.899	0.534	0.500	[27]

a and c are the lattice constants; u is an internal coordinate of h-WO₃ which fixes the relative position of the anion and cation sublattice along the c axis



Fig. 1 The band structure of h-WO₃ a, total DOS of h-WO₃ b, PDOSs of W c, O d atoms for h-WO₃

total DOS of bulk WO₃ is shown in Fig. 1b, and the partial density of the states (PDOS) of O and W atoms is exhibited in Fig. 1c, d. PDOS of O and W atoms indicates that the conduction band (CB) of WO₃ is mainly contributed by Op and Ws electronic states and that the valence band (VB) is mainly contributed by Op and Wd electronic states. As discussed hereafter, our results are sufficiently accurate to interpret qualitatively the resistivity measurements [29, 30].

3.1 Adsorption of HCHO on W and O Sites of WO-Terminated h-WO₃ (001) Surface

HCHO molecule may be adsorbed on W or O sites of WOterminated h-WO₃ (001) surface (denoted as HCHO–W₅ and HCOH–O₇, respectively). The calculated model is shown in Fig. 2. Figure 2a, b shows the crystal structure and (001) surface of h-WO₃, respectively. For the HCHO– W₅ configuration (Fig. 2c), the HCHO molecule is pushed far away from the (001) surface, and the distance between O atom of HCHO and W₅ is 0.2474 nm after adsorption. As measured in HCHO molecule, the C=O double bond with a length of 0.1221 nm has no change compared with that of free HCHO molecule (0.1219 nm), as listed in Table 2. The length of C-H bond changed from 0.109 to 0.1111 nm. The geometric construction of (001) surface and the bond angle of O-C-H₁ of HCHO only have a little difference compared with those before adsorption. The adsorption energy of HCHO-W5 configuration is calculated to -0.309 eV, which indicates the adsorption of HCHO molecule on W site of (001) surface can be taken place spontaneously. Figure 2d shows the HCOH-O7 configuration. It can be found that the bond angle of H₁-C-H₂ and O–C–H₂ of HCHO has been hardly changed after adsorption on O site of (001) surface and its adsorption energy is calculated to -0.432 eV, which indicates the adsorption of HCHO molecule on WO-terminated (001) surface is a physical adsorption [21]. Apparently, the adsorption of HCHO molecule on O site is also spontaneous. The distance between O₇ and H atoms around 0.2356 nm



Fig. 2 Crystal structure of h-WO₃ **a**, clean WO-terminated h-WO₃ (001) surface after optimizing **b**, and optimized adsorption structures of HCHO on W_5 (HCHO– W_5 configuration) **c**, O_7 (HCOH– O_7 configuration) **d** site of WO-terminated h-WO₃ (001) surface, respectively

Configuration	Bond angle (°)		Bond leng	Bond length/atomic distance (Å)				
	OCH1	O-C-H ₂	H ₁ -C-H ₂	C=O	C–H ₁	C-H ₂			
НСНО	121.889	121.889	116.223	1.219	1.116	1.116			
HCHO-W5	121.369	121.365	117.266	1.221	1.110	1.111	O-W ₅ (2.474)		
HCOH-O7	121.175	119.879	118.942	1.234	1.103	1.113	H ₁ -O ₇ (2.356)		
HCOH–O ₁₆	110.039	126.835	116.347	1.207	2.024	1.098	H ₁ -O ₁₆ (0.986)		

Table 2 The bond angle and bond length or atomic distance for optimized free HCHO molecule and three HCHO-adsorbed configurations

can be observed in HCOH– O_7 configuration. Due to the close of the adsorbed distance and adsorption energy for HCHO– W_5 and HCOH– O_7 configuration, two adsorption forms may be existed simultaneously.

The DOS of HCHO-adsorbed WO₃ (001) surface is shown in Fig. 3a (HCHO–W₅) and 3c (HCOH–O₇). New energy levels can be observed in HCHO-adsorbed (001) surface at around -6.5 and -10 eV. The PDOSs (Fig. 3b, d) of C and O atoms indicate the variation of DOS should be ascribed to the interaction between C 2*p* and O 2*p* orbitals of HCHO molecule and atoms of WO₃ (001) surface.

To investigate electronic structure of $h-WO_3$ (001) surface, the electron density difference (EDD) of the clean (001) surface and HCHO-adsorbed (001) surface was further analyzed. Figure 4a–c shows the EDD of the clean

(001) surface and HCHO-adsorbed (001) surface. As observed in the marked area (blue circle), electronic structure of the clean (001) surface (Fig. 4a) is slightly different from that of the HCHO-adsorbed (001) surface (Fig. 4b, c). It implies the electron density of HCHO molecule has changed before and after adsorption. It can be ascribed to the charge transfer between HCHO molecule and WO₃ (001) surface after adsorption [22].

In order to explore the sensing mechanism and elucidate the sensitive property of h-WO₃ to the HCHO gas, Mulliken populations of HCHO and WO₃ (001) surface were analyzed. These results are listed in Tables 3 and 4. It can be found that the free HCHO molecule is electrically neutral before adsorption. After adsorption, for HCHO–W₅ configuration (Table 3), the total Mulliken charge on



Fig. 3 Total density of the states of HCHO– W_5 a and HCOH– O_7 b configurations; PDOSs of C and O atoms of HCHO molecule for HCHO– W_5 c, HCOH– O_7 d configurations

HCHO molecule changes from 0 to 0.15e, which indicates the HCHO molecule as a unity losses 0.15e charges transferred to WO_3 (001) surface. The transferred charges are from O (losing 0.05e) and H (losing 0.12e) atoms of HCHO. Most of the transferred charges are obtained by WO_3 (001) surface atoms (0.15e). The W_5 atom and other atoms of (001) surface obtain the charge with 0.09e and 0.07e, which confirms the electronic structure of WO₃ (001) surface effected by adsorption of the HCHO molecule, as represented in EDD of (001) surface (Fig. 4b). In the case of HCOH–O₇ configuration, 0.12e charges transfer from HCHO molecule to WO₃ (001) surface. As shown in Table 4, the lost charges come from O (losing 0.07e) and H_2 (losing 0.08*e*) atoms of HCHO. The charges transferred to (001) surfaces are obtained totally by atoms around the O₇ atom. As a result of gain of charges, the resistance of h-WO₃ will be decreased [31, 32]. Therefore, h-WO₃ materials may have a good sensitivity to HCHO gas.

3.2 Adsorption of HCHO on O Sites of O-Terminated h-WO₃ (001) Surface

For O-terminated h-WO₃ (001) surface, HCHO molecule can be adsorbed on O sites (denoted as HCOH–O₁₆). Figure 5a, b shows the clean O-terminated h-WO₃ (001) surface and the optimized HCOH–O₁₆ configuration, respectively. For the case of HCHO–O₁₆ configuration, the calculated adsorption energy is -1.936 eV which is larger than those of HCHO–W₅ and HCOH–O₇ configurations. It implies the adsorption of HCHO molecule on O-terminated (001) surface is a chemisorption process. This conjecture is further confirmed by the optimized adsorption structure of HCHO on



Fig. 4 The calculated electron density difference of the clean (001) surface \mathbf{a} , HCHO-absorbed (001) surface for HCHO-W₅ \mathbf{b} , HCOH-O₇ \mathbf{c} configurations

Table 3 The Mulliken population analysis for HCHO-W₅ configuration before and after HCHO adsorption

Atom	Before a	adsorption				After ac	lsorption			
	S	р	d	Total	Charge (e)	S	р	d	Total	Charge (e)
0	1.84	4.64		6.48	-0.48	1.78	4.65		6.43	-0.43
С	1.26	2.80		4.06	-0.06	1.28	2.80		4.08	-0.08
H_1	0.73			0.73	0.27	0.67			0.67	0.33
H_2	0.73			0.73	0.27	0.67			0.67	0.33
W ₅	2.32	6.26	3.64	12.22	1.78	2.34	6.31	3.66	12.31	1.69

Table 4 The Mulliken population analysis for HCOH-O₇ configuration before and after HCHO adsorption

Atom	Before a	adsorption				After ad	sorption			
	S	р	d	Total	Charge (<i>e</i>)	S	р	d	Total	Charge (e)
0	1.84	4.64		6.48	-0.48	1.82	4.59		6.41	-0.41
С	1.26	2.80		4.06	-0.06	1.28	2.79		4.07	-0.07
H_1	0.73			0.73	0.27	0.75			0.75	0.25
H_2	0.73			0.73	0.27	0.65			0.65	0.35
O ₇	1.86	4.83		6.69	-0.69	1.85	4.84		6.69	-0.69

O-terminated (001) surface. As observed in optimized HCOH– O_{16} configuration (side view, Fig. 5c), the distances of W_5 – O_{16} and C– H_1 bonds increase from 0.1975 and 0.109 to 0.2667 and 0.202 nm, respectively. It can be speculated that the ruptures of O_{16} – W_5 and C– H_1 bonds should be occurred after the adsorption of HCHO molecule. Meanwhile, the distance between O_{16} and H_1 atoms is 0.0986 nm which is close to that of O–H bond (0.098 nm), indicating the formation of O–H bond. Furthermore, the angle of C– O_{16} – H_1 is

measured to be 106.043°, which is also closed to that of optimized HCOOH molecule (107.162°, shown in Fig. 5d). Concluding from the large adsorption energy and optimized adsorption structure for HCOH– O_{16} configurations, the oxidation of HCHO to form HCOOH occurred. These will be further verified by DOS analyses of O-terminated (001) surface before and after HCHO adsorption.

To understand the variation of the electronic structure, DOS of $HCOH-O_{16}$ configuration was investigated. As



Fig. 5 Clean O-terminated h-WO₃ (001) surface \mathbf{a} ; optimized adsorption structures of HCHO on O₁₆ (HCOH–O₁₆ configuration) \mathbf{b} ; magnified image as marked with *black ellipse* in \mathbf{b} image \mathbf{c} ; optimized structure for HCOOH molecule \mathbf{d}



Fig. 6 Total density of states of HCOH– O_{16} configurations **a**; PDOSs of C and O_{16} atoms after adsorption **b**; PDOSs of O_{16} and W_5 atoms before and after adsorption **c**; PDOSs of C and H₁ atoms before and after adsorption **d**

Atom	Before a	adsorption				After ad	sorption			
	S	р	d	Total	Charge (e)	S	р	d	Total	Charge (e)
0	1.84	4.64		6.48	-0.48	1.85	4.74		6.59	-0.59
С	1.26	2.80		4.06	-0.06	1.08	2.55		3.63	0.38
H_1	0.73			0.73	0.27	0.5			0.5	0.5
H_2	0.73			0.73	0.27	0.64			0.64	0.36
O ₁₆	1.86	4.83		6.69	-0.69	1.83	4.83		6.66	-0.66

Table 5 The Mulliken population analysis for HCOH $-O_{16}$ configuration before and after HCHO adsorption

shown in Fig. 6a, an obvious difference is observed in DOS before and after the adsorption of HCHO, which suggests that adsorbed HCHO molecule has an important influence on the electronic structure of O-terminated (001) surface. Figure 6b shows the PDOSs of C and O₁₆ atoms. A large population of overlap between C 2p and O₁₆ 2p orbitals indicates the formation of C-O₁₆ bond. Figure 6c shows the PDOSs of O₁₆ and W₅ atoms before and after HCHO adsorption. The overlap between $O_{16} 2p$ and $W_5 5d$ orbitals decreases obviously in the range of 0-5 eV after HCHO adsorption which implies the rupture of O₁₆-W₅ bond of O-terminated (001) surface. Similarly, the PDOSs of C and H₁ atoms are also analyzed. As shown in Fig. 6d, the decrease in the peak intensity from 5 to 10 eV indicates the interaction between C 2p and H1s orbitals was weakened after HCHO adsorption. The orbitals' overlap at ca. -3 eVis disappeared, which further suggests the rupture of $C-H_1$ bond of HCHO. These analysis results confirm the oxidation of HCHO to HCOOH on O-terminated h-WO₃ (001) surface and the change of electronic structure of O-terminated (001) surface.

The Mulliken population of HCHO molecule before and after adsorption is listed in Table 5. The transferred charge between HCHO molecule and O-terminated (001) surface is 0.65*e*, which is much higher than that between HCHO molecule and WO-terminated (001) surface. It indicates O-terminated (001) surface has much higher reactivity to HCHO than that of WO-terminated (001) surface. As shown in Table 3, the most of the transferred charges are from C (0.44*e*) and H₁ (0.23*e*) atoms, which implies the great change for the electronic structure of C and H₁ atoms, as shown in Fig. 5d. Therefore, the O-terminated (001) h-WO₃ surface has much higher sensitivity to HCHO gas.

4 Conclusions

Adsorption of HCHO molecule on h-WO₃ (001) surface was investigated using the first-principles calculation based on the DFT. Three HCHO-adsorbed configurations were considered. For adsorption on WO-terminated (001) surface or O-terminated (001) surface, the calculated results indicated that all adsorption configurations including HCHO–W₅, HCOH–O₇, and HCOH–O₁₆ can be formed spontaneously. The DOS of WO-terminated and O-terminated h-WO₃ (001) surface would change after HCHO adsorption, which implied the electrical properties of (001) surface would be influenced due to the adsorption of HCHO. Mulliken populations for three HCHO-adsorbed configurations verified that the charge transfer was occurred between HCHO and h-WO₃ (001) surface. These results suggested that h-WO₃-based materials could be as a candidate for application in HCHO gas sensing.

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References

- Y. Suzuki, N. Nakano, K. Suzuki, Environ. Sci. Technol. 37, 5695 (2003)
- [2] Z. Wang, J. Liu, F. Wang, S. Chen, H. Luo, X. Yu, J. Phys. Chem. C 114, 13577 (2010)
- [3] B. Geng, C. Fang, F. Zhan, N. Yu, Small 4, 1337 (2008)
- [4] M. Epifani, E. Comini, R. Díaz, J. Arbiol, P. Siciliano, G. Sberveglieri, J. Morante, Sens. Actuators B 118, 105 (2006)
- [5] G. Korotcenkov, Mater. Sci. Eng. B 139, 1 (2007)
- [6] M. Ippommatsu, H. Ohnishi, H. Sasaki, T. Matsumoto, J. Appl. Phys. 69, 8368 (1991)
- [7] L. Deng, X. Ding, D. Zeng, S. Tian, H. Li, C. Xie, Sens. Actuators B 163, 260 (2012)
- [8] M. Law, H. Kind, B. Messer, F. Kim, P. Yang, Angew. Chem. Int. Ed. 114, 2511 (2002)
- [9] E. Comini, G. Faglia, G. Sberveglieri, Z. Pan, Z. Wang, Appl. Phys. Lett. 81, 1869 (2002)
- [10] Y. Wang, X. Jiang, Y. Xia, J. Am. Chem. Soc. 125, 16176 (2003)
- [11] Y. Qin, X. Li, F. Wang, M. Hu, J. Alloys Compd. 509, 8401 (2011)
- [12] D. Hua, M. Liu, Y. Qin, J. Alloys Compd. 587, 227 (2014)
- [13] M. Ahsana, T. Tesfamichaela, M. Ionescub, J. Bella, N. Mottaa, Sens. Actuators B 162, 14 (2012)
- [14] C. MateiGhimbeu, M. Lumbreras, M. Siadat, J. Schoonman, Mater. Sci. Semicond. Process. 13, 1 (2010)

- [15] J. Wang, P. Zhang, J. Qi, P. Yao, Actuators B 136, 399 (2009)
- [16] S. Pokhrel, C. Simion, V. Teodorescu, N. Barsan, U. Weimar, Adv. Funct. Mater. 19, 1767 (2009)
- [17] Y. Xu, Z. Tang, Z. Zhang, Y. Ji, Z. Zhou, Sens. Lett. 6, 938 (2008)
- [18] I. Szilágyi, S. Saukko, J. Mizsei, P. Király, G. Tárkányi, A. Tóth, A. Szabó, K. Varga-Josepovits, J. Madarász, G. Pokol, Mater. Sci. Forum 589, 161 (2008)
- [19] I. Szilágyia, L. Wang, P. Gouma, C. Balázsi, J. Madarász, G. Pokold, Mater. Res. Bull. 44, 505 (2009)
- [20] C. Wang, F. Wang, X. Fu, E. Zhang, Z. Xu, Chin. Phys. B 20, 210 (2011)
- [21] L. Zhao, F. Tian, X. Wang, W. Zhao, A. Fu, Y. Shen, S. Chen, S. Yu, Comput. Mater. Sci. 79, 691 (2013)
- [22] Z. Zhao, X. He, J. Yi, C. Ma, Y. Cao, J. Qiu, RSC Adv. 3, 84 (2013)
- [23] B. Sun, W. Chen, J. Zheng, C. Lu, Appl. Surf. Sci. 255, 3141 (2008)

- [24] J. Scaranto, S. Giorgianni, Mol. Phys. 106, 2425 (2008)
- [25] X. Wang, F. Tian, W. Zhao, A. Fu, L. Zhao, Comput. Mater. Sci. 68, 218 (2013)
 [26] B. Ingham, S. Hendy, S. Chong, J. Tallon, Phys. Rev. B 72,
- [20] B. Ingnam, S. Hendy, S. Chong, J. Tallon, Phys. Rev. B 72, 075109 (2005)
- [27] B. Gerand, G. Novogorocki, J. Guenot, M. Figlarz, J. Solid, State Chem. 29, 429 (1979)
- [28] A. Kaushal, D. Kaur, J. Nanopart. Res. 13, 2485 (2011)
- [29] C. Filippi, D. Singh, C. Umrigar, Phys. Rev. B 50, 14947 (1994)
 [30] C. Lambert-Mauriat, V. Oison, J. Phys. Condens. Matter 18, 7361 (2006)
- [31] Y. Shi, M. Wang, C. Hong, Z. Yang, J. Deng, X. Song, L. Wang, J. Shao, H. Liu, Y. Ding, Sens. Actuators B 177, 1027 (2013)
- [32] Y. Xue, Z. Tang, Sens. Actuators B 138, 108 (2009)