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https://doi.org/10.15017/1906405

出版情報：Proceedings of International Exchange and Innovation Conference on Engineering & Sciences (IEICES). 3, pp.135-136, 2017-10-19. Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Effect of UV irradiation on nonanal adsorption on ZnO nanowire array

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Abstract: *Nonanal is a typical exhaled breath biomarker for lung cancer diagnosis. Surface adsorption of nonanal is the key process when using metal oxide semiconductor gas sensor to discriminate nonanal molecules. In this study, different wavelength of UV light is adopted to investigate the effect of UV irradiation on nonanal adsorption on ZnO nanowire array by FT-IR. The result indicates that UV irradiation can be as an effective method to activate strong chemical bonding. In addition, the wavelength of UV light has strong influence on the bond mode of nonanal on ZnO surface. 260 nm UV light possesses the best adsorption performance.*

Keywords: nonanal, UV light, ZnO nanowire

1. INTRODUCTION

Lung cancer is one of the most serious malignancies with rapidly growing rates of morbidity and mortality. Efficient early diagnosis is the best protection against lung cancer [1]. In this effort, exhaled breath analysis system should be a potential choice due to its non-invasive diagnostic approach [2]. It is well known that nonanal can be a typical biomarker for lung cancer diagnosis [3]. But it is difficult to effectively detect nonanal from exhaled breath because of the vast number of VOCs species in breath samples. The traditional thermally-driven chemiresistive gas sensors have already been commercial and used to detect some VOCs. But their poor selectively and accuracy limit their application in medical field [4]. However, considering their merits of miniaturization and facial operation, they still can be an alternative after some improvement. Ultraviolet light irradiation should be an available method to improve the performance of chemiresistive gas sensor. But most works are focus on the decrease of power dissipation by instead of thermally-driven [5]. The research about about the effect of UV light on selectivity is rarely reported. As the basic of gas detection, surface adsorption of gas molecules on sensing material is the key process. Exploring the effect of UV irradiation on nonanal adsorption is extremely important for realizing the discrimination of nonanal molecules using UV irradiation.

Therefore, in this work, ZnO nanowire array is chosen as the sensing material since it has direct wide band gap (E_g~3.3eV) and simple crystal-growth technology [6]. Different wavelength of UV light (dark, 260, 300 and 350 nm) is adopted. The result indicates UV irradiation can influence nonanal adsorption on ZnO nanowire array. The adsorption type can be adjusted by turning the wavelength of UV light, which proves that UV light can be a potential method for enhancing the selectivity of chemiresistive gas sensor.

2. EXPERIMENTAL SECTION

Preparation of ZnO nanowire array. Si wafer coated with ZnO seed layer (RF sputtering, 50W, 3min) was used as substrate to grow ZnO nanowire array by a hydrothermal method. First, 25mM of $Zn(NO_3)_2 \cdot 6H_2O$ and hexamethylenetetramine (HMT) were dissolved in 100 mL of deionized water. Then 2.5 mM of PEI and 3mL of $NH_3 \cdot H_2O$ were added into above solution in turn. The Si wafer coated with ZnO seed layer was immersed in the solution and kept at 95 °C for 10 h. The as-grown sample was rinsed in deionized water, and then dried in air. Then the as-grown ZnO sample was annealed at 600 °C for 1h in air. The crystalline structures of the samples were investigated using X-ray diffraction. The morphology was observed by field emission scanning electron microscopy (FESEM).

Nonanal adsorption on ZnO nanowire array. 2 μL of nonanal was dropt on the ZnO nanowire array (size: 1 cm×1.5 cm) and dried by nitrogen gas to remove the un-adsorbed nonanal molecules. Different wavelength of UV light (dark, 260, 300 and 350 nm) was adopted to irradiate the samples for different time. FTIR transmission spectra were used to investigate the phenomenon of nonanal adsorption under UV irradiation.

3. RESULTS AND DISSCUSION

3.1 Structural and Morphological Characteristics.

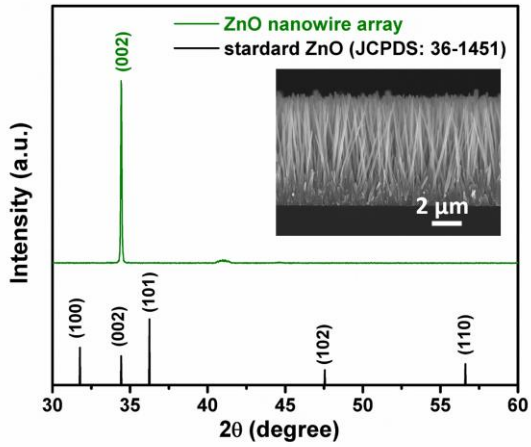

Fig. 1. XRD spectrum and SEM image of ZnO nanowire array.

X-ray diffraction (XRD) was conducted to identify the composition and crystalline phase of the final products. As shown in Fig.1, the (002) peak is clearly seen at

34.42°. The diffraction peak could be indexed to a wurtzite hexagonal ZnO structure (JCPDS Card No. 36-1451). No other diffraction peaks could be observed, which indicated that the as-grown ZnO samples were grown along the c-axis.

The inset of Fig. 1 shows the cross sectional SEM image of the as grown ZnO samples. Well-aligned ZnO nanowire array was produced and highly perpendicular to the Si substrate. The length and diameter were also very uniform (length: ~7.5 µm, diameter: 80~120 nm).

3.2 Effect of UV irradiation on nonanal adsorption.

Ultraviolet light can be as the energy source to drive the nonanal adsorption on ZnO nanowire array. In this section, different wavelength of UV light (dark, 260, 300 and 350 nm) is adopted and the time-dependent FT-IR results are shown in Fig. 2.

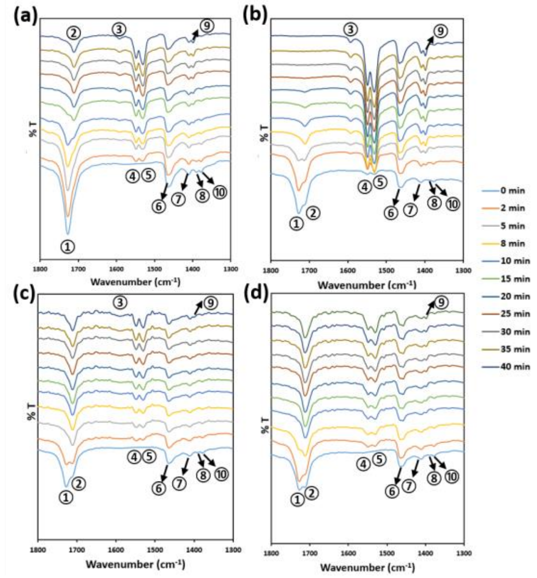

Fig. 2. Time dependent FT-IR spectra of nonanal adsorption on ZnO nanowire array under dark (a), 260nm (b), 300nm (c) and 350nm (d) UV light irradiation.

Table 1. FT-IR peak position index in Fig. 2.

No.	Wavenumber(cm^{-1})	Vibration modes
① ②	1727 1711	V_s(C=O)
③ ④ ⑤	1592 1549 1530	V_{as}(COO)
⑥	1467	δ (CH_2/CH_3)
⑦	1410	δ (CH_2/CH_3)
⑧	1390	δ (CH) from CHO
⑨	1399	V_s(COO)
⑩	1378	$δ_s(CH_3)$

In addition, the relevant FT-IR peak position index is summarized in Table 1. Obviously, the transformation of peak ① to peak ② can be observed no matter under dark or UV irradiation. This phenomenon may be due to C=O initially weakly bond with surface exposed lattice Zn atom. Then according to the decrease of peak V_s(C=O) and the increase of peak V_{as}(COO), as well as the disappear of peak ⑧, we can get the information that the group –C-H in R-CHO is broken and gradually transform to carboxylate R-COO-Zn to adsorb on the surface of ZnO. The peak ③, ④ and ⑤ all belong to V_{as}(COO), but the adsorption configuration is different. From current result, the UV irradiation may only affect the speed of transformation from R-CHO to R-COO-Zn in adsorption process. Fig. 3 records the variation trend of V_s(C=O) and V_{as}(COO) (1549 cm^{-1}) peak intensities with time from 0 to 40 min. The result indicates that that 260 nm UV light has the best promotion for this transformation. In addition, the transformation tends to saturation after a certain time for dark, 300 nm and 350 nm.

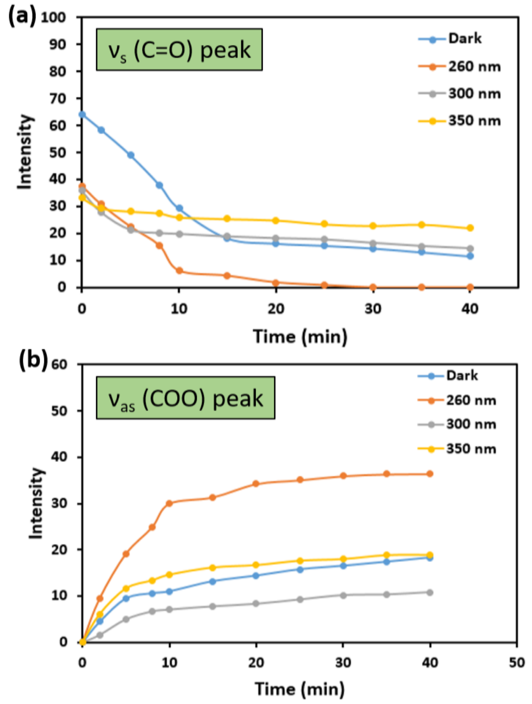

Fig. 3. Variation trend of V_s(C=O) and V_{as}(COO) (1549 cm^{-1}) peak intensities with time from 0 to 40 min.

4. CONCLUSION

In summary, the adsorption behavior of nonanal on ZnO nanowire array was successfully investigated using FT-IR spectrum. The influence of UV irradiation was explored by changing wavelength and designing time dependent experiment. In comparison to dark condition, UV irradiation can be used to tailor the adsorption behavior of nonanal by selecting suitable wavelength of light, which give a guideline for developing the discrimination of nonanal from exhaled breath.

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