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Molecular imprinted oxide coated ZnO nanowires pre-concentrator for separating nonanal from volatile organic compounds

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Abstract: *In this work, a robust molecular fingerprinting of metal oxide nanowires selectively to recognizes nonanal gas as target molecule from analogous volatile molecule mixture is successfully prepared. The functional material is composed of zinc oxide (ZnO) nanowires with titanium oxide shell. ZnO nanowires were prepared by hydrothermal methods and the fingerprint shell layer was obtained by sol-gel method. The molecular imprinted nanowires could highly recognize the nonanal gas among different functional group in the mix C9 gases. Also, the selectivity among different chain length is measured and weak selectivity could be observed. Such result shows the fingerprint process could imprint C=O bond and recognition C=O bond. The present concept based on volatile molecules via molecular fingerprinting of oxide nanowires will be an interesting approach to integrate a selective molecule sensor on integrated electronics and utilized in human breath.*

Keywords: Nanowires, ZnO, selectivity, nonanal

1. INTRODUCTION

Human breath contains large amount of information that show the healthy state of individual. Such as in hepatitis's breath, NH_3 concentration is much higher than normal human, and diabetes mellitus have higher amount CH_3COCH_3 . In recent years, nonanal has been proved to be an effective biomarker for early lung cancer detect [1-3]. Therefore, nonanal gas detective become a focus in the sensing field. Nowadays researchers had successfully make some sensor for detecting nonanal gas, but there is still an inherent difficulty for the conventional sensors to selectively detect a target molecule species from volatile molecule mixture since sensors gain electric signals via electrostatic and/or charge transfer interaction with functional groups of molecules, selectivity of different gas with analogous structure and chemistry properties with nonanal haven't been reported. [3-6]

Molecular imprinting means induce target template and make link-cross around the target template. After chemically and/or thermally treatment and remove the template molecule, a molecular recognition function is available. Nowadays molecule imprinted skill is a powerful approach to fabricate a molecular recognition space Therefore, a discrimination performance of volatile molecule sensing would be drastically enhanced by combining the molecular imprinting technique to the sensor devices. [7] the molecular recognition space is less effective to the volatile molecules with small number of recognition sites. In this study, we fabricated a molecular fingerprint using titanium oxide based material onto zinc oxide (ZnO) nanowires by introducing nonanal as a template molecule.

EXPERIMENTAL PROCEDURES

The molecularly fingerprinted oxide nanowires were synthesized by the following process. First, ZnO seed layer with 5nm thickness was deposited onto Si (100) substrate by radio frequency (RF) sputtering with power

of 100 W and Ar gas pressure of 0.3 Pa for 3 min. Then, the ZnO nanowires were grown from the seed layer by a hydrothermal method. The nanowire growth solution was the mixture of hexamethylenetetramine (HMTA), zinc nitrate hexahydrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2.5 mM polyethyleneimine (PEI) and deionized (DI) water and stirring for 5 min at room temperature. The ZnO nanowire growth was carried out in an oven at 95 °C for 24 h. After the nanowire growth, Ti layer was deposited by RF sputtering with a power of 50 W and an Ar pressure of 0.3 Pa for 30 min, followed by oxygen plasma treatment to form titanium oxide (TiOx) intermediate layer. Finally, the molecularly fingerprinted titanium oxide was formed onto the TiOx coated ZnO nanowires by alkoxide based sol-gel technique. The sol was confected by mixing precursor-tetrabutyl titanate, dealcoholization catalyst agent-titanium (IV) chloride and template molecule-nonanal at 60 °C for 1 h. Then the sol was spin-coated on the nanowires with 4000 rpm of rotation speed for 1 min, and finally the sample was further baked at 400 °C for 1 h to completely remove the incorporated template molecules.

3. RESULTS AND DISCUSSION

Figure 1 shows a typical field emission scanning electron microscopy (FESEM) image of the molecularly fingerprinted oxide nanowires grown onto Si substrate. The nanowires are uniformly distributed on the substrate. The diameter, length and number density of nanowires are ca. 100 nm, 3 μm and 35 wires/ m^2 , respectively. From this figure, after molecule imprint process, the surface structure changed, and it could be observed obviously. The length of molecule imprint nanowire is the same as ZnO nanowire, but the diameter increased, which means the molecule fingerprint ZnO nanowire was fabricated successfully.

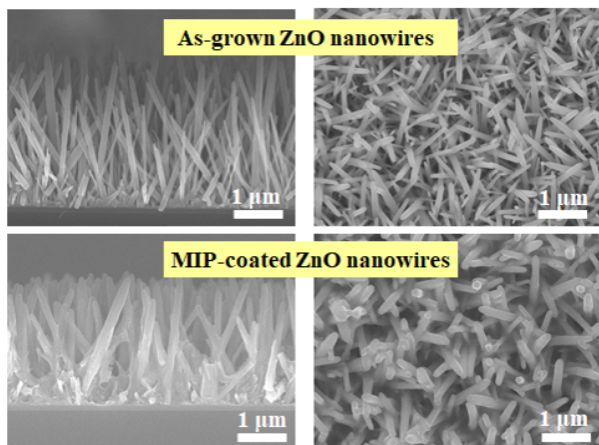


Figure 1. Field emission scanning electron microscopy (FESEM) image of the molecularly fingerprinted oxide nanowires.

Figure 2 shows the GC-MS (Gas chromatography–mass spectrometry) result of MIO (Molecule imprint oxide) nanowire and NIO (Non-molecule imprint oxide) nanowire after mix gas adsorption. The mix gases include nonane, 2-nonanone, nonanal, 1-nonanol and nonanoic acid. In the spectrum, no nonanoic acid could be observed. This scenario may cause by the low nonanoic acid adsorption amount or nonanoic acid peak is wide and low, hard to detect. Except nonanoic acid, the adsorption amount of nonane and 1- nonanol is nearly same in MIO and NIO nanowires. This demonstrated that the template molecule has no influence to the nonane and 1- nonanol adsorption process. As for 2-nonanone and nonanal gas, the adsorption amount of MIO nanowire is two times higher than NIO nanowires. This phenomenon demonstrates the imprint is successfully to C=O bond recognition.

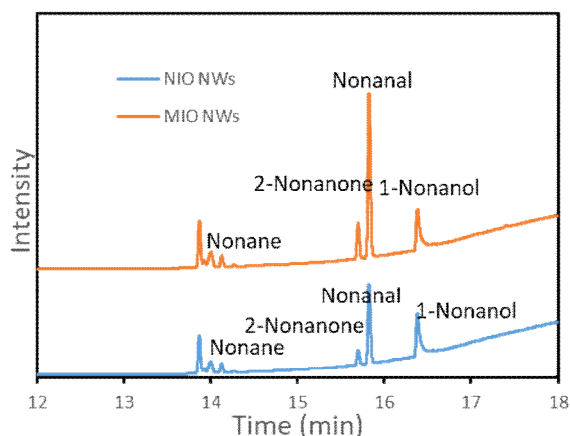


Figure 2. TIC result of MIO (Molecule imprint oxide) nanowire and NIO (Non-molecule imprint oxide) nanowire after mix gas adsorption.

Figure 3 shows the adsorption amount in mix gas and in each single gas. From this figure, the adsorption amount of each gas in mix gas and in single gas is nearly same, no big fluctuate. The result demonstrates the adsorption process is single, the influence between different kind of gases could be ignored. Each kin of gas adsorption are independence. The nonanal adsorption amount enhancement is really cause by the fingerprint process.

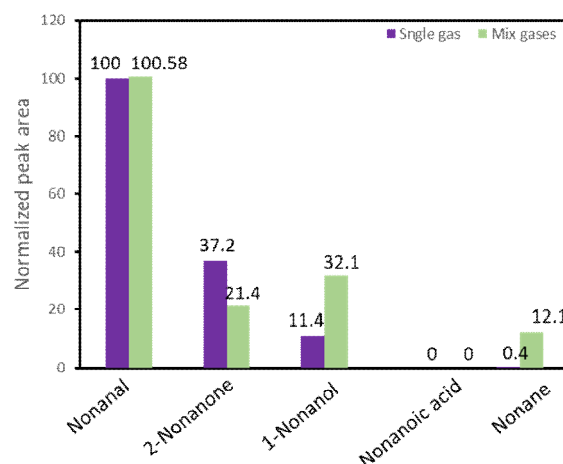


Figure 3. adsorption amount in mix gas and in each single gas

4. CONCLUSION

The molecular imprinted nanowires could highly recognize the nonanal gas among different functional group in the mix C9 gases. Such result shows the fingerprint process could imprint C=O bond and recognition C=O bond. The present concept based on volatile molecules via molecular fingerprinting of oxide nanowires will be an interesting approach to integrate a selective molecule sensor on integrated electronics and utilized in human breath.

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