Vol 4 | Issue 1 | Pages 117-121

Advances in Metallurgical and Material Engineering

ISSN: 2689-8705

Research Article

DOI: 10.36959/508/402

Strontium Barium Titanates Nanowires Sensors: Preparation and Application in Prediction of Cancers by Exhaled Biomarkers

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Abstract

$Sr_{0.6}Ba_{0.4}TiO_3$, $SrTiO_3$, $BaTiO_3$ nanowires were synthesized by hydrothermal method with all-inorganic raw materials and without any pH adjustment, organic precursors or templates, high temperature. The width of nanowires is 25-150 nm, the length is ten to hundred of micrometers. The array of sensors based on $Sr_{0.6}Ba_{0.4}TiO_3$, $SrTiO_3$ and $BaTiO_3$ nanowires was designed without any organic modifier. The array of sensors can distinguish the simulated cancers breath from healthy breath without the need for pre-concentration and dehumidification, accounts for > 98% variance. Nine volatile organic compounds that represent lung, liver, kidney, breast, diabetes cancers were used to train and optimize the sensors. Our results show that the array of sensors with a detection limit of ppt level is a low-cost, simple, rapid, sensitivity and non-invasive sensing technology, much simpler and lower detection limit than the gold nanoparticles sensors and colorimetric sensor.

Introduction

Volatile organic compounds (VOCs) generated by the human body have been much studied, especially in breath analysis. A number of VOCs in breath, e.g., ammonia [1,2], ketones [3], ethanol [2], propanol [4], pentane and hexane etc. of C_4-C_{11} straight or monomethylated alkanes [5,6], benzene derivatives [7], have been identified as biomarkers of different systemic diseases, such as lung, liver, kidney, diabetes and breast cancers. The breath analysis has been proposed as a fast, convenient, non-invasive and painlessness procedure, complementary to blood and urine sampling [8-10]. Gas chromatography/mass spectrometry (GC-MS) [11,12], selected ion flow tube mass spectroscopy [3], laser adsorption spectrometry [13], infrared spectrometry [14], surface acoustic wave sensors [15,16] and coated quartz crystal microbalance sensors [17] have been used for this purpose. However, these techniques are expensive, slow, require complex instrument and, further more, require pre-concentration of the biomarkers.

Here, we report $Sr_{0.6}Ba_{0.4}TiO_3$, $SrTiO_3$, $BaTiO_3$ nanowires were synthesized by hydrothermal methods. The synthesis involves low-cost, all-inorganic raw materials, unlike solid-state, sol-gel and other hydrothermal synthesis employing high temperature, organic precursors, pH adjustment [18-20]. The array of sensors based on $Sr_{0.6}Ba_{0.4}TiO_3$ nanowires was designed and can distinguish the breath of cancers from the breath of healthy individuals without the need for pre-concentration and dehumidification.

Experimetal Methods

Hydrothermal synthesis of $Sr_{0.6}Ba_{0.4}TiO_3$, $SrTiO_3$, $BaTiO_3$ nanowires from $Na_2Ti_3O_7$ nanowires

The $Na_2Ti_3O_7$ nanowires have been prepared by the hydrothermal method, 0.20g of TiO_2 powder (Degussa P25) was mixed with a NaOH (Alfa Aesar) aqueous solution (concentration of 10 mol/L) and placed in a 150 mL poly(tetrafluoroethylene) lined autoclave, ultrasonic for 20 min. The synthesis was performed at 240 °C for 3 days. The products were isolated by centrifugation and washed several times with distilled water until pH of 7 and then dried at 60 °C overnight.

$Sr_{0.6}Ba_{0.4}TiO_3$, $SrTiO_3$ and $BaTiO_3$ nanowires were synthesized by the reaction of $Na_2Ti_3O_7$ with $Sr(OH)_2$ (Alfa Aesar) or $Ba(OH)_2$ (Alfa Aesar) under a hydrothermal condition. A typical preparation procedure of $Sr_{0.6}Ba_{0.4}TiO_3$ is shown as follows:

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Accepted: May 21, 2021

Published online: May 23, 2021

Citation: Xing K, Ryan TZ, Wang M (2021) Strontium Barium Titanates Nanowires Sensors: Preparation and Application in Prediction of Cancers by Exhaled Biomarkers. Adv Metallurg Mater Eng 4(1):117-121

0.04 g of $Na_2Ti_3O_7$ nanowires, 0.02g $Sr(OH)_2$, 0.10g $Ba(OH)_2$ and 10 mL DDW (deionized distilled water) were mixed and put into the 50 mL Teflon-lined autoclave. The autoclave was placed into an oven at 150 °C for 3 days. After reaction, the autoclave was cooled down to room temperature and the $Sr_{0.6}Ba_{0.4}TiO_3$ nanowires were separated by centrifugation and repeatedly washed with 0.1 M aqueous nitric acid, centrifugalized and thoroughly washed with distilled water several times, and finally dried at 60 °C overnight.

Material characterization

The crystal structure and phase composition of the synthesized $Sr_{0.6}Ba_{0.4}TiO_3$, $SrTiO_3$, $BaTiO_3$ and $Na_2Ti_3O_7$ nanowires were characterized by X-ray diffraction (XRD, MiniFlex Rigaku) using CuKa radiation. Scanning electron microscope (SEM), Energy-dispersive X-ray analyses (EDX) and transmission electron microscopy (TEM) were carried out on Philips ESEM XL30 microscope and Titan STEM80-300, respectively.

Fabrication of the sensor

The nanowires were mixed with DDW in a weight ratio of 10:1 to form sensing film. The sensing film was drop-cast onto a silicon substrate (4 mm × 4 mm) with gold interdigital electrode and dried in oven at 60 °C overnight. Each electrode has 40 fingers, fingers width and gap distance is 25 µm, the thickness of the gold is about 2000 angstroms. The structure of sensor is shown in Figure 1 and Figure 2.

Simulation and test of breathe samples

Nine VOCs [1-7] were attained by dissolving ammonium hydroxide, acetic acid, ethanol, toluene, methylhydrazine, pentane, hexane, isopropanol and acetone solution into distilled water, respectively. Each compound's concentration is 5 ppt, 5 ppb and 5 ppm. The healthy breath and cancers breath were simulated by mixing the nine compounds into solution with each compound's concentration of 10 ppb and

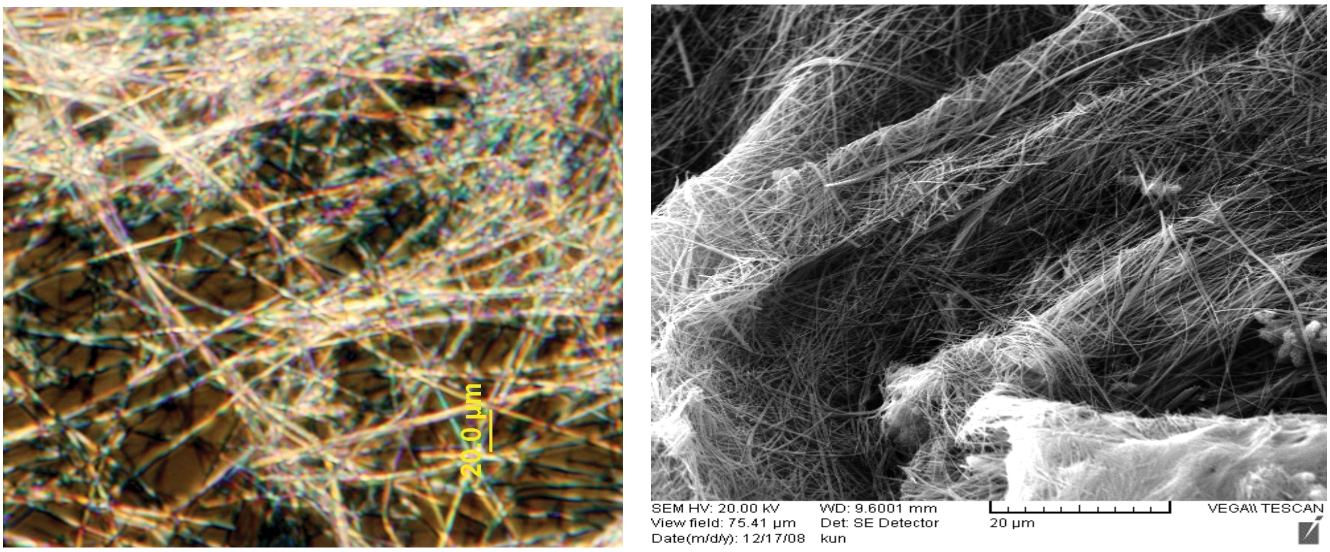

Figure 1: Electric Microscope and SEM of $Sr_{0.6}Ba_{0.4}TiO_3$ nanowires.

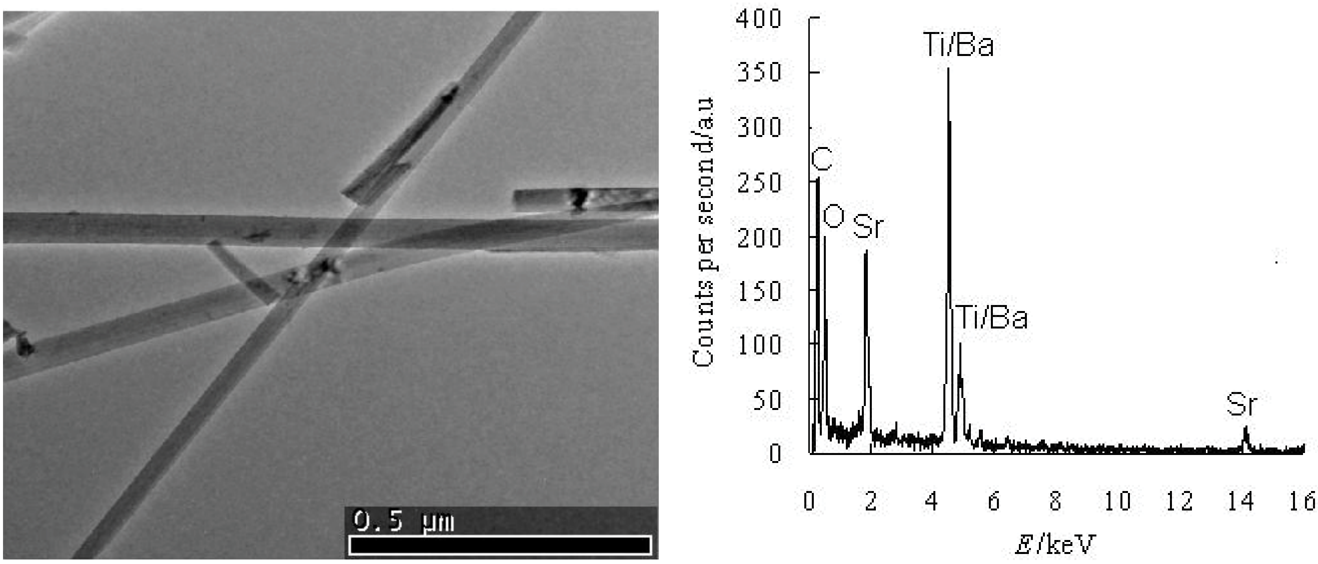

Figure 2: TEM and EDS of $Sr_{0.6}Ba_{0.4}TiO_3$ nanowires.

100 ppb, respectively. The resistance values (*R*) of samples were measured using a SR810 DSP Lock-In Amplifier at room temperature (about 23 °C) and 100 Hz.

Results and Discussion

Material characterization

The XRD patterns of $Sr_{0.6}Ba_{0.4}TiO_3$, $SrTiO_3$, $BaTiO_3$ and $Na_2Ti_3O_7$ are shown in Figure 3. It is observed that all the peaks fit well to the peak positions of layered sodium titanate [21,22] (JCPDS No.31-1329), cubic phase $SrTiO_3$ [18-20] (JCPDS No.35-734) and $BaTiO_3$ [20,23] (JCPDS No.31-174), respectively. The peak positions of $Sr_{0.6}Ba_{0.4}TiO_3$ (d_{110}, $2\vartheta = 31.8$) locate between $BaTiO_3$ (d_{110}, $2\vartheta = 31.6$) and $SrTiO_3$ (d_{110}, $2\vartheta = 32.4$). The energy dispersive X-ray spectroscope (EDS) analysis in Figure 2 from different positions along one single nanowire shows that the nanowires are essentially composed of Sr, Ba, Ti and O. The element molar ratio of Sr and Ba is 6:4, which indicates that the molecular formula is $Sr_{0.6}Ba_{0.4}TiO_3$. From the patterns of $Sr_{0.6}Ba_{0.4}TiO_3$, $SrTiO_3$ and $BaTiO_3$, no peaks of $Na_2Ti_3O_7$ can be found, it indicates that the layered structure of $Na_2Ti_3O_7$ has been lost and relatively complete reaction between the $Na_2Ti_3O_7$ and Sr $(OH)_2$ or $Ba(OH)_2$ takes place. The results demonstrate that pure $Sr_{0.6}Ba_{0.4}TiO_3$, $SrTiO_3$ and $BaTiO_3$ nanowires can be attained by hydrothermal method from $Na_2Ti_3O_7$ nanowires. The processes involve all-inorganic raw materi-

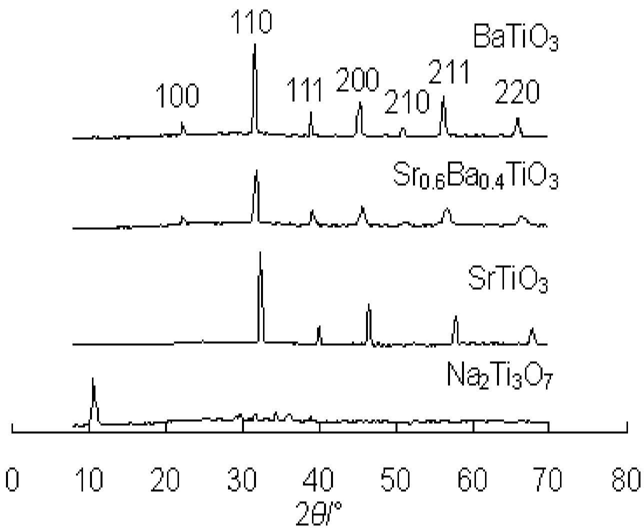

Figure 3: XRD patterns of $Sr_{0.6}Ba_{0.4}TiO_3$, $SrTiO_3$, $BaTiO_3$ and $Na_2Ti_3O_7$ nanowires.

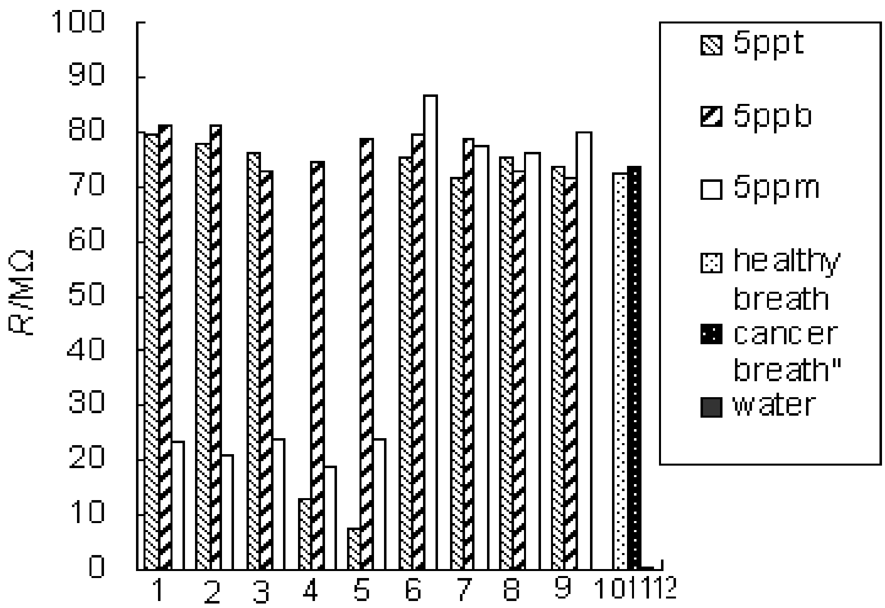

Figure 4: Diagnosis breath biomarkers using $Sr_{0.6}Ba_{0.4}TiO_3$ sensor.

Remark: 1. Ammonia; 2. HAc; 3. Ethanol; 4. Toluene; 5. Methylhydrazine; 6. Pentane; 7. Hexane; 8. Isopropanol; 9. Acetone; 10. Simulated healthy breath; 11. Simulated cancers breathe; 12.Water moisture.

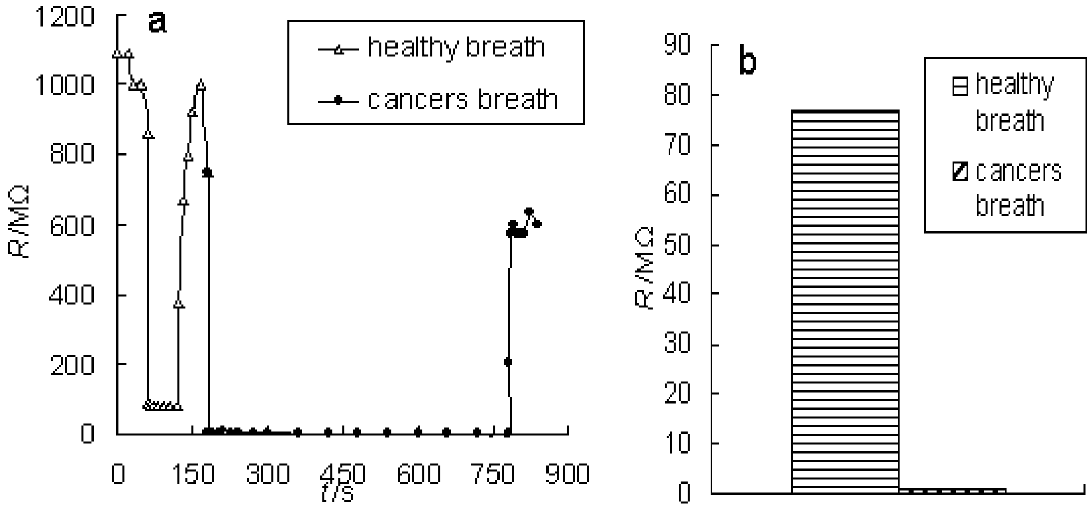

Figure 5: Distinguish the cancers breath from healthy breath using the array of sensors.

Remark: In the Figure 5a, the flat data curves indicate the sensor was exposed to the breath biomarkers, the other parts indicate the sensor was in the atmosphere.

als, without pH adjustment, organic precursors or templates, high temperature, not like recent report [18-24].

Electric Microscope, Representative scanning electron microscope (SEM) and transmission electron microscope (TEM) images are presented in Figure 1 and Figure 2. The images show that straight $Sr_{0.6}Ba_{0.4}TiO_3$ nanowires have a uniform cylindrical structure with diameters of 25-150 nm and the lengths from ten to one hundred micrometers.

Detection of breath biomarkers

The responses of the $Sr_{0.6}Ba_{0.4}TiO_3$ sensor to nine representative cancer biomarkers at different concentrations were investigated in Figure 4. The results show that the detection limit of sensor can arrive at ppt level, much below the concentration levels of these VOCs in the exhaled breath of cancerous patients. The responses are hardly affected by the presence of the water molecules. The sensor to methylhydrazine and toluene show a very different response at different concentration, but to other biomarkers or simulated breath of cancers and breath of healthy individuals, there is no clear difference.

In order to improve the sensitivity of the sensor, an array of sensors was designed by combing $Sr_{0.6}Ba_{0.4}TiO_3$, $SrTiO_3$ and $BaTiO_3$ sensors in series. The results in Figure 5a show that the response is rapid and reversible. Figure 5b shows a very big difference and no overlap between the simulated cancers and healthy patterns, accounts for > 98% variance. It can be seen that the array of sensors can distinguish the breath of cancers (lung, liver, kidney, breast and diabetes cancers) from the breath of healthy without the need for pre-concentration and dehumidification. The array of sensors was designed just by $Sr_{0.6}Ba_{0.4}TiO_3$, $SrTiO_3$ and $BaTiO_3$ nanowires without any organic modifier, pH adjustment, organic template or precursors, high temperature, much simpler and lower detection limit than the gold nanoparticle sensors [25] and colorimetric sensor [26]. The results demonstrate the array of the sensors is a low-cost, simple, rapid, sensitivity and non-invasive sensing technology for predicting the cancers.

Conclusion

$Sr_{0.6}Ba_{0.4}TiO_3$, $SrTiO_3$, $BaTiO_3$ nanowires were synthesized by hydrothermal method involves all-inorganic raw materials, without pH adjustment, organic template or precursors, high temperature. The width of nanowires is 25-150 nm, the length is ten to hundred of micrometers.

The array of sensors based on $Sr_{0.6}Ba_{0.4}TiO_{3,}$ $SrTiO_3$ and $BaTiO_3$ nanowires is a simple, inexpensive, rapid, sensitive and non-invasive sensing technology for predicting the cancers. It can rapidly distinguish the simulated breath of cancers patients (lung, liver, kidney, diabetes, breast cancers) from the breath of healthy individuals, accounts for > 98% variance, without the need for pre-concentration and dehumidification. The detection limit of the array of sensors is low to ppt level. The array of sensors was designed just by $Sr_{0.6}Ba_{0.4}TiO_{3,}$ $SrTiO_3$ and $BaTiO_3$ nanowires without any organic modifier, pH adjustment, organic template or precursors, high temperature, much simpler and lower detection limit than the recent report.

Acknowlegement

The authors thank David Paul for helpful instructions and suppling the SR810 DSP Lock-In Amplifier. This work was supported by China Scholarship Council.

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DOI: 10.36959/508/402