Talanta 120 (2014) 408–412

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Characterization of an array of Love-wave gas sensors developed using electrospinning technique to deposit nanofibers as sensitive layers

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ARTICLE INFO

Article history:
Received 9 October 2013
Received in revised form
8 December 2013
Accepted 11 December 2013
Available online 21 December 2013

Keywords:
Nanofibers
Love wave
Gas sensor
Chemical warfare agent
Sensor array
Electrospinning

ABSTRACT

The electrospinning technique has allowed that very different materials are deposited as sensitive layers on Love-wave devices forming a low cost and successful sensor array. Their excellent sensitivity, good linearity and short response time are reported in this paper. Several materials have been used to produce the nanofibers: polymers as Polyvinyl alcohol (PVA), Polyvinylpyrrolidone (PVP) and Polystirene (PS); composites with polymers as PVA+$SnCl_4$; combined polymers as PS+Poly(styrene-alt-maleic anhydride) (PS+PSMA) and metal oxides (SnO_2). In order to test the array, well-known chemical warfare agent simulants (CWAs) have been chosen among the volatile organic compounds due to their importance in the security field. Very low concentrations of these compounds have been detected by the array, such as 0.2 ppm of DMMP, a simulant of sarin nerve gas, and 1 ppm of DPGME, a simulant of nitrogen mustard. Additionally, the CWA simulants used in the experiment have been discriminated and classified using pattern recognition techniques, such as principal component analysis and artificial neural networks.

1. Introduction

Arrays of acoustic wave devices (AW) [1–3] have widely been used in sensing applications. Some types of acoustic wave sensors are quartz crystal microbalances [4–6], devices based on Rayleigh waves [7–10] and Love waves [11–13]. The AW devices can be functionalized using a great variety of materials as sensitive layers, such as polymers [4–11], metal oxides [13,14], and nanotubes [15,16], which are deposited on the active area of the AW device in order to adsorb the volatile organic compounds (VOC). The morphology of the sensing layer plays an important role in the molecular adsorption–desorption process, sensor response and therefore in the sensitivity. In recent years, nanostructured materials have been under research in many fields and are also promising to be used as sensing materials due to their large surface to volume ratio which provides high surface area. The nanostructured materials can be used as sensitive layers in AW devices instead of a thin layer, improving the sensitivity and velocity of the response due to their great reaction surface. Therefore, sensitive layers of nanostructured materials can provide higher sensitivity and lower insertion losses than the sensitive thin films coated with methods such as drop, airbrush spray or spinning.

Several reports about nanofibers as sensitive layer of AW sensors have been published [17,18] and there is an increase in the use of the electrospinning technique to deposit them on AW sensors [19–21]. The electrospinning is a simple, efficient and low cost method to deposit nanofibers of very different materials [22–28] since the selectivity and sensitivity of a sensor to a target VOC are very dependent on its chemical and physical properties. Therefore, it is possible to use combinations of a great variety of materials as sensitive layers in order to make efficient arrays of sensors.

The combination of Love-wave devices with different elecstrospun nanofibers can provide substantial advantages to detect VOCs, such as higher sensitivity and selectivity, and lower insertion losses of the devices. However, as far as we know, there are no references of the use of an array of Love-wave devices with electrospun nanofibers to detect VOCs; therefore, it has been made an array consisting of six sensors with different electrospun nanofibers as sensitive layers.

Among the VOCs, chemical warfare agents (CWA) such as nerve, vesicant, incapacitating, lacrimator or emetic agents have been selected, since they are powerful weapons used to kill or incapacitate humans, being a threat to public safety. Due to the above reasons, there is an urgent interest in developing highly

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http://dx.doi.org/10.1016/j.talanta.2013.12.027

sensitive, selective and quick devices to make an early detection system that is capable of detecting low concentrations of CWAs. Therefore, the array of AW sensors, which has been made in this work, has been tested with different concentrations of CWA simulants below the median lethal dose (LD_{50}: dose required to kill half the members of a tested population) of CWA, achieving to improve the performance of this type of sensors. Discrimination and classification of these gases are analyzed and discussed at the end of this paper.

2. Material and methods

2.1. Love-wave device

The SAW devices used in this work were of Love-wave type. They were based on a shear horizontal surface acoustic wave (SH-SAW) propagated on the ST-cut quartz substrate, perpendicular to the x crystallographic axis. This SH-SAW, with a wavelength of $\lambda = 28$ μm, was generated and detected by interdigital transducers (IDTs). The IDTs were made using standard lithographic techniques, depositing an aluminum layer with a thickness of 200 nm by RF sputtering and forming a delay line (DL). A double electrode structure was repeated 75 times to form each IDT. The distance center to center between IDTs was 225 λ and the acoustic aperture was 75 λ.

Finally, the Love-wave was obtained by guiding the SH-SAW in a film of SiO_2 deposited on the piezoelectric substrate by PECVD. The highest sensitivity was found for a thickness of SiO_2 of 3.5 μm, the synchronous frequency being around 163 MHz [12].

The sensors were electrically characterized by means of a vector network analyzer (Agilent 5070B) which measured the frequency response before and after the deposit of the electrospun fibers on the device. Next, each sensor was incorporated, as usually, to an oscillator circuit whose characteristics were measured by a spectrum analyzer (Agilent 9320A).

2.2. Electrospinning process

Electrospinning is a versatile technique for the preparation of continuous nanofibers. Sensitive materials prepared by this method have great potential in the field of the sensors by their large surface to volume ratio, provided by their three-dimensional nanoporous skeleton structure. In the electrospinning process, the solution in the syringe is extruded from the needle tip to the collector, where the device is placed. When high voltage is applied between the needle and the collector, an electrostatic force is induced on the droplets of the solution at the needle tip. The interaction between this electrostatic force and the surface tension causes the droplets to stretch, forming thin jets of polymer solution that dry during flight and are deposited on the collector. If any of the electrospinning parameters, such as the applied voltage, needle-to-collector distance, solution viscosity, or flow rate of solution is changed, the morphology of the fibers obtained on the collector may be affected.

The setup for electrospinning consisted of a 10 ml glass syringe with a metallic needle screwed on the tip. The syringe was filled with polymer solutions, and then placed in the syringe pump (NE-1000), which allowed controlling the flow velocity of the polymer solution. The needle was connected to a high-voltage power supply and was directed to a copper plate which served as the grounded collector, where the Love device was placed. In this way random fibers were produced by the high applied voltage between the needle and the collector (which forms a homogenous electric field), coating with the sensing materials on the device surface.

2.3. Preparation of polymers using electrospinning

The electrospinning technique allows us to obtain nanofibers of composites created by mixing different polymers or additional materials, thereby making it possible to build up an array of sensors with high sensitivity and selectivity. An array of six sensors was developed in this study using the following polymers as sensitive materials:

- *Polyvinyl alcohol (PVA)* is a water soluble polymer produced industrially by hydrolysis of poly(vinyl acetate) and is commercially available in different molecular weights. It has high chemical stability and, due to its excellent physical and mechanical properties, is broadly used in practical applications as fiber and film products, paper coatings, adhesives and contact lens or artificial organs. In our work, PVA samples (Sigma-Aldrich) with two different molecular weights and different composite formations were deposited onto three of our Love-wave sensors.
  The first PVA solution, 10% w/v, was prepared by dissolving PVA (Mw ~94,000 g/mol) powder in deionized water and stirring at 90 °C during 4 h. After cooling to room temperature, it was loaded into the syringe to be deposited as sensitive film onto the surface of the sensor S1 of the array, using the parameters shown in Table 1.
  A second solution was prepared from a PVA / $SnCl_4 \cdot 5H_2O$ composite. A solution of PVA (Mw ~170,000 g/mol) was prepared by dissolving the PVA powder 8% w/v in deionized water and stirring it at 90 °C for 4 h. A solution of 2 g of tin (IV) chloride pentahidrate ($SnCl_4 \cdot 5H_2O$) (Sigma-Aldrich) with 2 g of deionized H_2O was also prepared at room temperature. This solution was slowly added to 20 g of PVA solution and stirred at room temperature for 2 h. The resulting inorganic/organic composite solution was loaded into a syringe to be deposited using the parameters shown in Table 1, and it was deposited onto the surface of the sensors S2 and S3 of the array. Finally, the sensor S2 with the electrospun fibers was introduced into a tube furnace at a temperature of 450 °C for 4 h in ambient atmosphere, obtaining nanowires of SnO_2.
- *Polystyrene (PS)* is a synthetic resin produced by the polymerization of the styrene. It is a waterproof and low thermal conductor. Polystyrene is used extensively in many industries and is the base material for many products. It is one of the most common plastics used in everyday life.
  First, a polymer solution was prepared for electrospinning by dissolving a mixture of PS (Mw ~192,000 g/mol) (Sigma-Aldrich) and the copolymer Poly(styrene-alt-maleic anhydride) (PSMA) (Mw ~350,000 g/mol) (Sigma-Aldrich) at a 2:1 weight ratio in *N*,*N*-dimethylformamide (DMF) solvent. The total

Table 1
Electrospun parameters for preparation of the nanofibers of the polymers used. V is the high voltage applied, ν is the flow rate of the syringe pump, d is the needle-to-collector distance, Ø is the external diameter of the needle, t is the time of electrospinning and D is the average of the diameters of the fibers.

Sensor	Electrospun nanofiber	V (kV)	ν (μl·min^{-1})	d (cm)	Ø (mm)	t (seg)	D (nm)
S1	PVA[a]	19.5	12	10	0.6	25	~150
S2	PVA[b]+$SnCl_4$ Annealing 4 h 450 °C	19	5	10	0.6	300	~100
S3	PVA[b]+$SnCl_4$	19	5	10	0.6	300	~250
S4	PS+PSMA	18	5	20	0.6	20	~800
S5	PS	18	5	20	0.6	30	~800
S6	PVP	18	5	22	1.1	60	~200

[a] PVA (Mw~94,000 g/mol).
[b] PVA (Mw~170,000 g/mol).