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Reliable detection of UDMH in sub-ppb level in variable atmospheric conditions by temperature modulated FSP-made SnO_2 and Ru/SnO_2 nanocomposite based MOX sensors

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Abstract:
Reliable detection of hypertoxic rocket fuel propellant – unsymmetrical dimethylhydrazine (UDMH) –with low rate of either false negative or positive signals in variable ambient air conditions by single temperature modulated semiconductor metal oxide sensor (MOX sensor) is presented. The applied sensitive materials are pure and Ru loaded nanocrystalline SnO_2 made by single step technique, known as flame spray pyrolysis. The machine learning algorithm was used for raw sensor data handling and processing.

Key words: metal oxide, semiconductor, gas sensor, UDMH, temperature modulation

Introduction

Rocket fuel propellant 1,1-dimethyl hydrazine is extreme toxic compound but is still at use in rocket and defense industry for its high energy of burning and easiness of handling and ignition in engines of upper-stage boosters in open space conditions. Current health and safety regulations put very low threshold limit values for UDMH vapor concentration in air either in working area or ambient atmosphere around – 40 and 0.4 ppb respectively (in Russia)[1]. Although, the wearable devices for aerial UDMH level control are present on the market, their reported lowest limit of detection is too high - around 20 ppb [2]. In the present work we demonstrate the possibility of application of MOX semiconductor sensors for the ecological control for extremely low concentration of hypertoxic compound - UDMH – below ppb level of concentrations.

Experimental

Sensor materials were synthesized by flame-spray pyrolysis technique. Tin II-ethylhexanoate and ruthenium(III) acetylacetonate were taken as precursors, which were dissolved in calculated amounts in toluene. This mixture was pulverized as aerosol through custom made nozzle by oxygen flow and ignited with support methane/oxygen flamelets. The mixture was fed with the rate of 5 ml/min, oxygen flow – 4 l/min. The condensed material was collected with Whatman GF/A glass filter (aided by the vacuum pump) situated 80 cm above the flame tip. The obtained material was annealed at 500 ^oC for 24 h. Pure SnO_2 material was synthesized according to the same protocol as a comparison sample. The obtained materials structure, morphology and chemical activity were studied by XRD phase analysis, TEM, BET and TPD-H_2 techniques. Sensors were made and preliminary gas sensing measurements towards 20 ppm of NH_3 in dry pure air were carried out with the use of synthesized materials as described elsewhere [3]. Sensing of UDMH vapor in sub-ppb level in air was carried out in an open chamber through which a constant flow of ambient air was generated by fan. A fixed concentration of UDMH in air flow was created through warm stainless-steel capillary tube, inserted in a chamber upstream of air flow (as shown on fig. 1) through which a flow of UDMH in nitrogen was added to air flow. A controlled concentration of UDMH in a nitrogen flow was created by thermostabilized permeation tube and additional amount of nitrogen flow, adjusted by mass-flow controller. During UDMH measurements sensors were operating in a temperature modulated mode with 150 and 500 ^oC as lower and upper limits of working temperature

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respectively, at which sensors were kept for 5 seconds. Linear heating and cooling stages of single temperature cycle lasted for 45 and 5 seconds respectively.

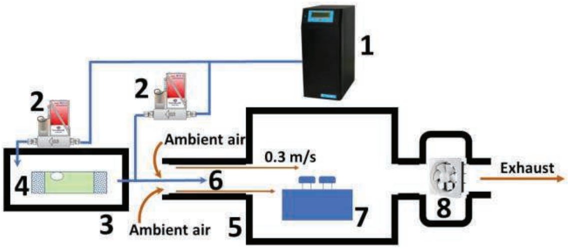

Fig.1 Set up for sub-ppb UDMH sensor measurements. 1 – pure nitrogen flow generator, 2 – MFCs, 3 – thermostat, 4 – thermostabilized UDMH permeation tube, 5 – open sensor chamber, 6 – UDMH inlet capillary stainless tube, 7 – electronic block for sensors temperature control and resistance measurements, 8 – ventilation fan.

Data was collected in several days during a month with various atmospheric pressure and air humidity, no filters and other techniques were used to improve the quality of urban air, used to dilute UDMH/N_2 mixture to sub-ppb levels. Several data processing techniques were applied to minimize negative effects of slow sensor resistance drift - polynomial detrending of whole experiment data - as well as noise and outliers of measurement equipment - subtraction of minimal value, normalization to integral value, moving average smoothing. For reliable determination of UDMH in air different machine learning models were trained on collected data samples. Train dataset consists of highly randomized samples of data ($2.7x10^3$ for air and UDMH in total for each UDMH concentration), recorded in different days to avoid any impact of atmospheric and sensor conditions on the inference of system (Fig.2).

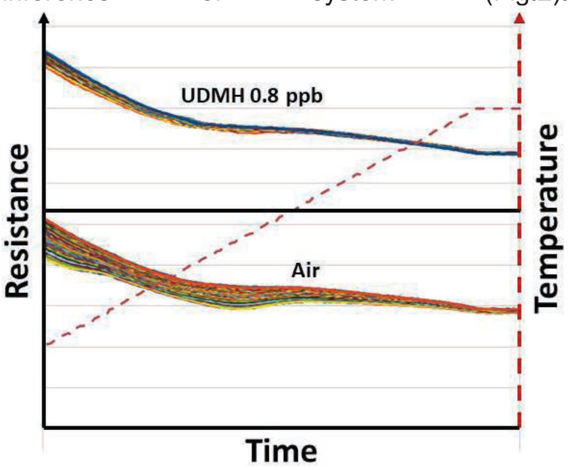

Fig. 2 Data samples for UDMH and air (150 each), used for machine learning. All parameters are in arbitrary units.

Also, we had to use statistical shape analysis approach (converting data to Kendall space and calculating shape-space distances) for the analysis of data, collected in highly variable ambient air.

Results

The obtained materials have approx. 15 nm sized grains and surface are of 29 and 35 m^2/g for pure and Ru-modified SnO_2 respectively. TPD-H_2 reflected significantly higher Red/Ox activity of Ru-modified SnO_2. Which resulted in a higher sensor response of this material to ammonia (Fig. 3).

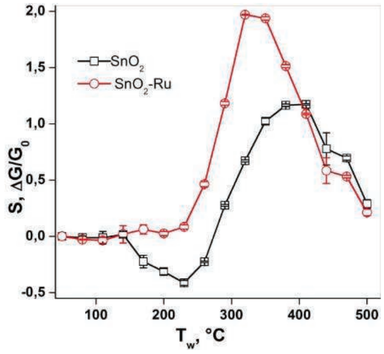

Fig.3 Sensor response towards NH_3 20 ppm in air.

Best result for UDMH detection – zero false negative answers even for 0.4 ppb concentration - was demonstrated for both sensors by deep neural networks with dropout regularization method and rmsprop as a gradient optimization method. A high degree of air variability, partially due to UDMH adsorption on sensor chamber walls, leads to the considerable number of false positive responses of the system – more than 30% for independent test data samples. However, methods of shape analysis allow to minimize these problems.

Conclusions

Reliable detection of sub-ppb concentrations of UDMH with low rate of false negative and positive signals is achievable by combination of flame spray pyrolysis made nanocrystalline SnO_2 based gas sensors and machine learning methods.

Acknowledgements

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