

Scope for the future work

Scope for the future work

9.0 Introduction	279
9.1 Chemical warfare	280
9.2 Chemical warfare/weapon agent (CWA)	280
9.3 CWA simulants	281
9.4 Preparation of simulant of CWA	282
9.5 Thin films by using USP (For nanostructured thin films)	283
9.6 Conclusions.....	284
References	285

Figure captions

Fig 9.1: Ultrasonic spray pyrolysis technique for the preparation of nanostructured thin films.

Table captions

Table 9.1: Examples of the highly toxic chemical agents.

Table 9.2: Agent, chemical gas, simulant and treatment to prepare their gas.

9.0 Introduction

In the present thesis, we have fabricated the spray pyrolysis set up for the preparation of pure and modified SnO₂ thin films. The prepared SnO₂ thin films were characterized by using different techniques such as XRD, SEM, AFM, TEM and UV-visible spectroscopy to correlate with their gas sensing performance towards hazardous and toxic conventional gases such as H₂S, NH₃, LPG, CO, CO₂, O₂, H₂, ethanol and Cl₂.

In this work we tried to prepare nanocrystalline thin films by using SPT. These films were analyzed and tested to various gases. The unique data and results have been published in referred journals. But to achieve monodispersed nanocrystalline materials and thin films remains a challenge for us. There are reports to prepare monodispersed nanocrystalline thin films by using ultrasonic spray pyrolysis (USP) technique [1]. Moreover, nowadays due to increased threat of international terrorism and their use of toxic chemical attack, societies need to pay more attention on protecting their citizens from attack of toxic chemicals, either by accident or terrorist act. Therefore fast detection and identification of toxic chemicals is crucial for efficient protection of citizens.

Therefore, it is our future aim to produce nanocrystalline thin films by using USP; and plan to test the chemical warfare agents.

The toxic chemical threats can be classified into two basic types: chemical warfare agents (CWA) and toxic industrial chemicals (TIC) as shown in detail in Table 9.1. Especially the threat of TICs has been widely realized in the recent years. That is due to their easy availability due to wide industrial use. Although CWAs are gradually more toxic and thus more dangerous than TICs, the CWA threat is reducing since in 1997 by more than 160 nations ratified the chemical weapons convention (CWC). That convention prohibits the development, production, stockpiling and use of CWAs as well as many of their precursors. Moreover, nations who are members of the Organization for the Prohibition of Chemical Weapons (OPCW) are banned from trading with nations, which did not sign the convention. Nevertheless, well-trained terrorists may still obtain chemical weapons - either by synthesizing themselves or from the nations which do not belong to the OPCW.

9.1 Chemical warfare

Chemical warfare (CW) involves using the toxic properties of chemical substances as weapons. This type of warfare is distinct from Nuclear warfare and Biological warfare, which together make up NBC, the military acronym for Nuclear, Biological, and Chemical (warfare or weapons). Neither of these falls under the term conventional weapons which are primarily effective due to their destructive potential. Chemical warfare does not depend upon explosive force to achieve an objective. Rather it depends upon the unique properties of the chemical agent weaponized. A lethal agent is designed to injure or incapacitate the enemy. Defoliants are used to quickly kill vegetation and deny its use for cover and concealment. It can also be used against agriculture and livestock to promote hunger and starvation. With proper protective equipment, training, and decontamination measures, the primary effects of chemical weapons can be overcome. Many nations possess vast stockpiles of weaponized agents in preparation for wartime use. The threat and the perceived threat have become strategic tools in planning both measures, and counter-measures.

9.2 Chemical warfare/weapon agent (CWA)

A chemical warfare/weapon agent (CWA) is a chemical substance whose toxic properties are used to kill, injure or incapacitate. About 70 different chemicals have been used or stockpiled as chemical weapon agents during the 20th century. These agents may be in liquid, gas or solid form.

Furthermore, in the case CWAs, OPCW provides 43 chemical groups or specific chemicals in three schedules. All together, the request for number of chemical agents to be detected and identified by CWA-TIC detector raises easily over 150 agents providing an extreme challenge for the detector developers. Fortunately, many suitable sensor and spectrometer technologies have been demonstrated and are also available in the market. Detectors deploy for example ion mobility spectrometers, IR spectrometers, flame photometric detectors, solid-state gas sensors and electrochemical sensors and their combinations. Basic key figures of these CWA-TIC detectors are detection, identification and quantification performance. Also response time can be considered as a key figure. Other favoured features are the capability of continuous operation, low weight, small size

and ease of operation. However, any of the CWA-TIC detectors available in the market today does not meet all the requirements regarding detection and identification performance and other technical challenges. Therefore, there is still significant need for further technology development.

Table 9.1: Examples of the highly toxic chemical agents.

CWA, chemical warfare agent	Nerve agents (e.g. sarin, soman, tabun and VX)
	Blister agents (e.g. sulfur mustard, lewisite)
	Choking and blood agents (e.g. phosgene, cyanide)
TIC, toxic industrial chemical	Common toxic chemicals e.g. ammonia, hydrogen cyanide, various inorganic acids, formaldehyde, chlorine
	Less-common highly toxic chemicals e.g. isocyanates, pesticides
	Less-toxic highly volatile chemicals e.g. benzene, toluene, acrylonitrile

9.3 CWA simulants

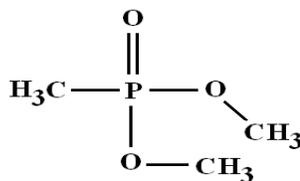
CWAs are highly toxic and their use is restricted. Research on the environmental fate of CWAs is often conducted using simulant compounds [2-11]. An ideal chemical agent simulant would mimic all relevant chemical and physical properties of the agent without its associated toxicological properties. Although a number of compounds have been used as CWA simulants, no individual compound is ideal because a single simulant cannot satisfactorily represent all environmental fate properties of a given CWA. Thus, a number of different chemicals have been used as CWA simulants depending on the physical and chemical properties of interest.

9.3.1 DMMP

Dimethyl methylphosphonate, or methylphosphonic acid dimethyl ester (DMMP), is a colorless liquid. It is combustible. It emits a distinct odour. It can be found in household radiators, especially those installed in the former Soviet Bloc. In contact with water it slowly undergoes hydrolysis. Dimethyl methylphosphonate is not classified as toxic, but is harmful if inhaled, swallowed or absorbed through the skin; it is a chemical used in the synthesis of sarin nerve gas. It can also be used as standalone as a simulant for sarin

training exercises and for calibration of detectors. It is a suspected carcinogen. Dimethyl methyl phosphonate (DMMP) is simulant of G-agent simulants [12].

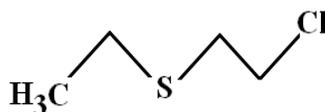
The chemical formula of DMMP is $C_3H_9O_3P$ or $CH_3PO(OCH_3)_2$ and represented as:



9.3.2 CEES

Chloroethyl ethyl sulfide (CEES) is simulant of Sulphur Mustard (HD). CEES contains a single chlorine atom on the β carbon relative to the sulfur atom (mustard is 2, 2-dichlorodiethyl sulfide). The 2-CEES molecule is much less toxic. Thus, it is expected that 2-CEES closely mimics the reactivity of mustard gas [13].

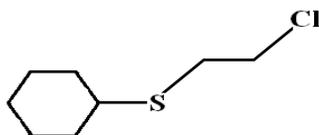
The chemical formula of CEES is C_4H_9ClS and represented as:



9.3.3 CEPS

2-chloroethyl phenyl sulfide (CEPS) is simulant of Distilled Mustard (HD). It is also called half-mustard (HM), to simulate HD in a study of CWA removal from water using activated carbon filters [14]. The CEPS molecule is much less toxic. Thus, it is expected that CEPS closely mimics the reactivity of mustard gas.

The chemical formula of CEPS is C_8H_9ClS and it is represented as:



9.4 Preparation of simulant of CWA

The real chemical warfare agents are very dangerous and difficult to handle. Therefore, simulants with very low toxicity or with no toxicity with similar chemical characteristics (shown in Table 9.2) were used to develop the sensors for their detection.

Table 9.2: Agent, chemical gas, simulant and treatment to prepare their gas.

Agent	Chemical gas	Simulant	Treatment	Simulant gas
Nerve	Sarin (GB)	dimethyl methyl phosphonate	Heating	DMMP
Blister	Distilled mustard (HD)	2-chloroethyl phenyl sulfide	Heating	CEPS
		2-chloroethyl ethyl sulfide	Heating	CEES

The simulants listed in Table 9.2 are in liquid phase. 0.5 μl of simulant to be tested was converted completely into vapors and maintained in vapor form by heating constantly at 70 $^{\circ}\text{C}$ in 250 ml airtight conical flask. With 0.5 μl of simulant in 250 ml airtight conical flask would be 2 ppm concentration of simulant. So obtained simulant (2 ppm) vapors were then used to test the sensors. The gaseous form (vapors) of 2 ppm simulant were injected in static sensing system using syringe having capacity of 20 ml and exposed on to the sensor surface at various temperatures.

9.5 Thin films by using USP (For nanostructured thin films)

Although, preparation of more focused narrow band nanostructured SnO_2 thin films is found to be a challenge. This challenge can be achieved by adopting sophisticated techniques such as ultrasonically preparation of thin films. There are reports regarding the ultrasonically prepared nanostructured MOS gas sensors.

The schematic block diagram of ultrasonic spray pyrolysis (USP) technique for thin film preparation is shown in the following Fig. 9.1, consist of: Bench table, Spraying chamber, X-Y scanner, Ultrasonic spray nozzle, Ultrasonic generator, Syring pump, Spraying solution, Glass substrate, Control panel, Electrical heater, Bronze block, Thermocouple, Temperature indicator, Exhaust fan.

Ultrasonic spray pyrolysis technique involves spraying a solution (fine mist or aerosol), usually aqueous, containing soluble salts of the constituents atoms of desired compound onto a substrate maintained at elevated temperature. The sprayed mist reaching a hot substrate surface undergoes pyrolytic decomposition and form a single crystallite or clusters of crystallites of product. The other volatile by-products and the excess solvent escape in the vapor phase. The substrate provides thermal energy for thermal decomposition and subsequent recombination of the constituent species followed by sintering and recrystallization of clusters of the crystallite giving rise to coherent film.

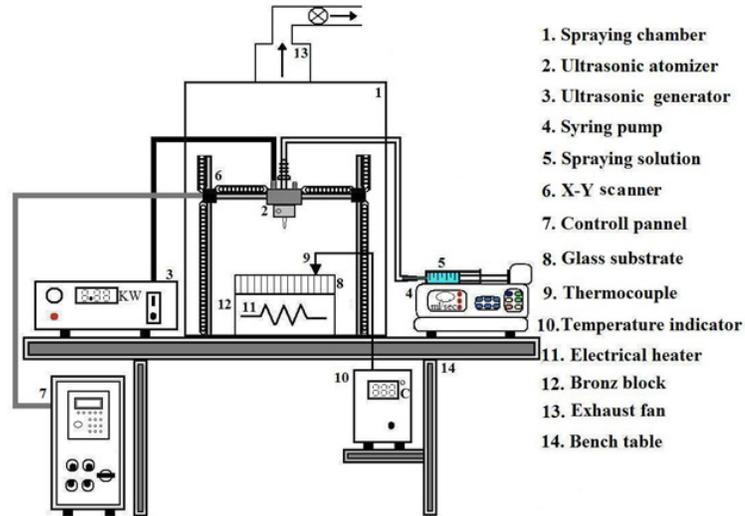


Fig. 9.1: Ultrasonic spray pyrolysis technique for the preparation of nanostructured thin films [15].

9.6 Conclusions

We successfully prepared pure and modified SnO₂ thin films and tested their gas sensing performance towards hazardous and toxic conventional gases such as H₂S, NH₃, LPG, CO, CO₂, O₂, H₂, ethanol and Cl₂. We tried to prepare nanocrystalline thin films by using SPT and tested their various properties with unique results; few of them are published in referred journals too. But we could not achieve the monodispersed nanocrystalline thin films by this SPT. So, it is our future aim to produce nanocrystalline thin films by using USP and try to detect the chemical warfare agents. Therefore, we are going to plan to prepare monodispersed nanocrystalline materials and thin films by using USP to overcome the difficulties encountered in the work which has been presented in the thesis.

References

- [1]. L. A. Patil, M. D. Shinde, A. R. Bari, V. V. Deo, *Sens. Actuator B* **143** (2009) 270.
- [2]. G. W. Wagner, B.W. Bartram, *Langmuir* **15** (1999) 811.
- [3]. C. L. Mangun, Z. Yue, J. Economy, *Chem. Mater.* **13** (2001) 2356.
- [4]. B.A.Tomkins, G. A. Sega, C. h. Ho, *J. Chromatogr. A* **909** (2001)13.
- [5]. Z. C. Yue, C. Mangun, J. Economy, P. Kemme, D. Crokek, S. Maloney, *Environ. Sci. Technol.* **35**(2001)2844.
- [6]. E. Raber, R. McGuire, *J. Haz. Mater.* **93** (2002) 339.
- [7]. V. T. Borrett, T. H. Gan, B. R. Lakeland, D. R. Leslie, R. J. Mathews, E. R. Mattsson, S. Riddell, V. Tantaro, *Chromatogr. A* **1003** (2003) 143.
- [8]. E. E. Seabolt, W.T. Ford, *Langmuir* **19** (2003) 5378.
- [9]. B. C. Singer, A. T. Hodgson, *Environ. Sci. Tech.* **39** (2005) 3203.
- [10]. F. C. G. Hoskin, J. E. Walker, *Bull. Environ. Contam. Toxicol.* **59** (1997) 9.
- [11]. G. W. Wagner, B. K. MacIver, *Langmuir* **14** (1998) 6930.
- [12]. E. Brunol, F. Berger, M. Fromm and R. Planade, *Sens. Actuators B* **120** (2006) 35.
- [13]. S. C. Stout, S. C. Larsen, V. H. Grassian, *Microporous and Mesoporous Mater.* **100** (2007) 77.
- [14]. Z. C. Yue, *Environ Sci. Technol* **35** (2001) 28448.
- [15]. L. A. Patil, A. R. Bari, M. D. Shinde, V. V. Deo, *Sens. Actuators B* **149** (2010) 79.
