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# Synthesis and characterization of magnetron sputtered $ZrO_2$ nanoparticles: Decontamination of 2-choloro ethyl ethyl sulphide and dimethyl methyl phosphonate

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ABSTRACT

The efficiency of $ZrO_2$ nanoparticles for the decontamination of 2-choro ethyl ethyl sulphide (CEES) and dimethyl methyl phosphonate (DMMP) has been studied. Nanoparticles have been synthesized using reactive magnetron sputtering technique and characterized using Powder XRD, FE-SEM, TEM, Raman spectroscopy, $N_2$-BET, TGA and FT-IR techniques. XRD patterns indicate that the as-deposited nanoparticles are amorphous in nature. After annealing at 300°, 450° and 600 °C, they transform from tetragonal to monoclinic phase. TEM analysis show that the particle size of the synthesized nanoparticle lie in the range of ~2–36 nm for as-deposited and annealed at various temperatures. The decontamination capability of these nanoparticles was studied using GC-FID and the reaction products were characterised by using GC–MS and FT-IR techniques. It was found that magnetron sputtered $ZrO_2$ nanoparticles exhibits better decontamination ability towards CEES and DMMP. The decontamination reactions exhibits pseudo first order kinetic behaviour with rate constant ($k$) and half life ($t_{1/2}$) values 0.178–0.107 $h^{-1}$ and 3.87–6.43 h for CEES and 0.034–0.015 $h^{-1}$ and 20.024–45.127 h for DMMP, respectively. The present study explored the role of hydrolysis and elimination reactions in the decontamination of CEES as well as in the decontamination of DMMP.



## 1. Introduction

Reactive sorbent composed of inorganic metal oxides nanomaterials demonstrate promising approach for the decontamination of chemical warfare agents (CWA) [1–5]. They possess high absorbability and enhanced reactivity in the application of environmental remediation and decontamination of CWA [6,7]. These interesting applications within the above materials are ascribed due to their higher surface area and the reactive acid, base sites that exist in the form of edges and corner defects, unusual lattice planes etc. [8–12].

Sulphur mustard (HD) and sarin (GB) are well known CWA and were effectively employed in the First and Second World War (WW I and WW-II) followed by its usage in several other incidents (e.g. in Gulf War and in Japan by terrorist). HD affects several organs of the human including skin, mucous membrane which causes blisters. It also alkylates guanine nucleotide in DNA and causes fatality to the cells. GB attacks on nervous transmission and block it permanently by binding with the acetylcholineesterase enzyme, causing paralysis and mortality. Therefore, decontamination of these CWA in the battle field conditions is a great challenge to the scientific community for the sake of national security [13]. For this purpose, several studies have been carried out for the decontamination of such warfare agent and as a consequence there exist number of decontaminant. Bleaching powder and potassium permanganate were the first reactive chemical decontaminants employed against CWA. *N*-chloro compounds (Chloramine-B, trichloisocyanuric acid, sodium *N*, *N*-dichloroisocyanurate, chloramine-T) were found to be promising decontaminants but due to lack of stability hindered their wide spread application [6]. Thereafter, decontamination solution DS2 was unleashed to replace ineffective bleaching solutions in colder environments. It is an organic formulation that has been found useful against a different number of CWA such as HD, GB, *O*-pinacolyl methyl phosphonofluoridate (GD), Ethyl *N*, *N*-dimethyl phosphoramidocyanidate (GA) and *O*-ethyl *S*-2-(diisopropylamino) ethyl methyl phosphonothioate. However, it causes corrosion to metal surfaces

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after prolonge contacts and softens. Later a number of oxidants such as *m*-chloro peroxy benzoic acid, magnesium monoperoxyphthalate, sodium-2-nitro-5 iodoxybenzoate, *o*-iodo benzoic acid and sodium hypochlorite were examined as active components along with surfactants in microemulsions for CWA decontamination [7–15] $H_2O_2$ and molybdenum salts, peroxy bicarbonate based aqueous decontaminants, $H_2O_2$ aerosols were used as decontaminants to neutralize the CWA [16,17]. But with liquid decontaminants have hydrophobic nature and are unable to remove them. Then, search for solid sorbent decontaminants such as Fullers earth, resin mixture (XE-555) and activated $Al_2O_3$ (A 200) by which most of the above problems minimized. The solid sorbent decontaminants were free of liquid and have high adsorbent capacity towards CWA to clean up the contaminated surface effectively. However, rate constant values of the above sorbent decontaminants with CWA was found to be very low compared to the liquid decontaminant. Also in comparison to the liquid decontaminant, the above sorbent did not clean up the contaminated area completely. Because of this, a search for the newer liquid free solid sorbent decontaminants is desirable that have high adsorbent capacity to adsorb the CWA agent strongly into its pores and converting them into non-toxic form.

A number of metal oxides such as CaO, $Al_2O_3$, $MnO_2$ nanobelts and nanostructures, $ZnO_2$ nanoparticles and nanorods, $Al_2O_3$ supported oxime, ferric oxide/graphite oxide composites, mixed metal oxides of $Al_2O_3$–$Fe_2O_3$, $Al_2O_3$–$V_2O_5$, $Al_2O_3$–CuO etc. have been reported for better decontamination properties towards CWA [14–22]. Kleinhammes et al. reported the decontamination of 2-chloro ethyl ethyl sulphide (CEES) on the surface of $TiO_2$ nanotubes through hydrolysis reactions [23]. Mahato et al. also studied the decontamination of GB, HD and CEES on the surface of $MnO_2$ nanobelts and found the degradation of them through hydrolysis reaction [16]. Aurian and Boucher [24] and Kanan and Tripp [25] reported the decontamination of dimethyl methyl phosphonate (DMMP) over the surface of metal oxides through hydrolysis reactions. Mattsson et al. and Stengl et al. reported the $Zr^{4+}$ doped metal oxides for the decontamination of CWA [26,27]. Recently, Verma et al. reported the degradation of CEES and DMMP on the surface of dc sputtered CuO and $WO_3$ nanoparticles through hydrolysis reactions [28,29]. The dc sputtered CuO nanoparticles displayed much better results in comparison to previously reported CuO nanoparticles and other metal oxides materials synthesized using chemical methods. Inspired by these results, we have chosen newer material having high adsorption capacity to degrade CWA with in few hours of duration to ensure the enhancement in the confidence levels regarding safety against the CWA.

In the current study we have chosen $ZrO_2$ nanoparticles because of its stability, non-toxicity, high strength and fracture toughness, high melting point, low thermal conductivity, high corrosion resistance, and high adsorption property [30,31]. Due to these unique properties $ZrO_2$ exhibited interesting applications in different research fields such as in gas-sensing, catalyst or catalyst support, photocatalysis and in wastewater treatment [32–35]. For the purpose of different applications $ZrO_2$ nanoparticles have been synthesized using different methods such as sol–gel process, hydrothermal route, precipitation process, thermal decomposition, and microwave irradiation [36–47]. In this work, we have

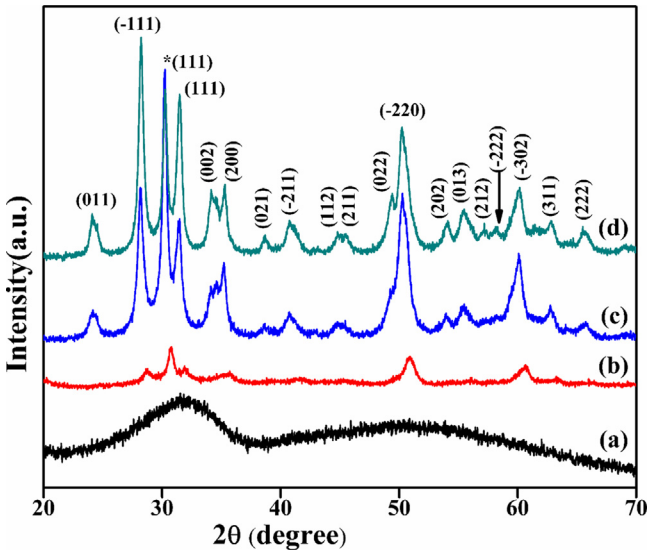


**Fig. 1.** XRD patterns of $ZrO_2$ nanoparticles (a) as-deposited and annealed at (b) 300 °C (c) 450 °C (d) and 600 °C.

synthesized $ZrO_2$ nanoparticles using reactive magnetron sputtering technique at very low temperature under highly controlled conditions for the removal and detoxification of CEES and DMMP. As expected it is a low cost decontamination technique. In water purification, this technique provides some important advantages such as high purity, narrow size distribution, uniformity and reproducibility over chemical synthetic methods [41]. Also this technique is capable to provide possible smallest particle size leading to large surface area as compared to reported in the literature. Inspired by these advantages, we have attempted to

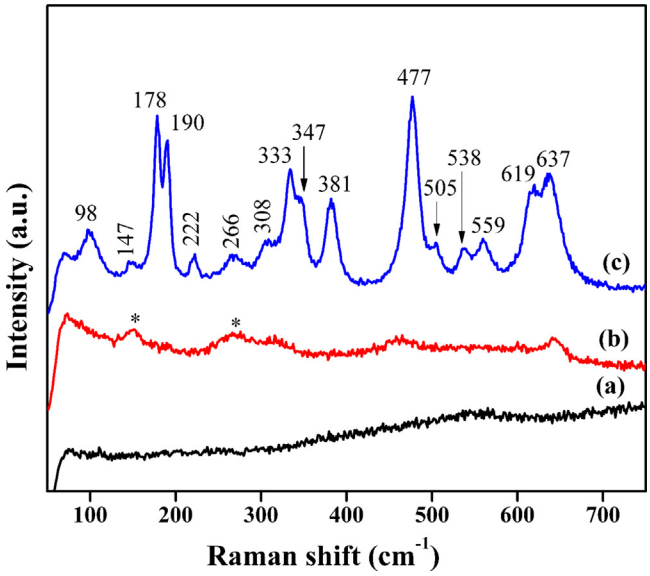


**Fig. 2.** Raman Spectra of $ZrO_2$ nanoparticles (a) as-deposited and annealed at (b) 300 °C and (c) 600 °C.

**Table 1**
Sputtering parameters for the synthesis of $ZrO_2$ nanoparticles.

| Target | Base pressure | Working pressure | Gas used | Deposition time | Distance (*d*) | Power (Watt) | Substrate temperature | Annealing temperature |
|---|---|---|---|---|---|---|---|---|
| Zr | $8.3 \times 10^{-7}$ Torr | 30 m Torr | Ar:$O_2$ ::40:5 | 72 h | 4.5 cm | 90 W | −194 °C | As-deposited, 300, 450, 600 °C |

*d* = Distance between target and substrate.