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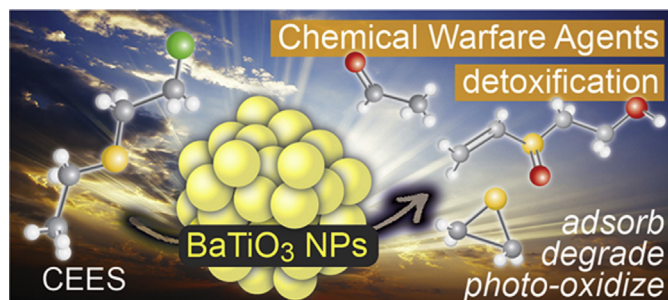
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Regular Article

Barium titanate perovskite nanoparticles as a photoreactive medium for chemical warfare agent detoxification

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GRAPHICAL ABSTRACT



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ABSTRACT

Barium titanate nanoparticles (BTO-NPs) in the size range 8–12 nm, prepared by gel collection, are found to be a photoreactive detoxifier for Chemical Warfare Agent vapors, specifically, the sulfur mustard surrogate (2-chloroethyl ethyl sulfide). The relatively monodisperse, uniformly spherical BTO-NPs, initially dispersed in alcohol solvents, form a stable and porous aggregated structure reminiscent of a nanostructured material with voids/pores of an average diameter of 4.6 nm and a relatively narrow distribution of their sizes (2.5–8.7 nm). Due to the interparticle porosity and a polar, chemically active surface, significant amounts of CWA surrogate and its decomposition products were adsorbed on the BTO-NPs. The recorded weight uptake on the perovskite was the highest among a series of materials and nanocomposites known for their detoxification activity and tested at the same conditions (169 mg/g, compared to 117 mg/g for zinc oxide and <100 mg/g for other transition metal oxides). Besides adsorption, BTO nanomaterial acts simultaneously as an efficient heterogeneous catalyst by degrading the toxic vapors to alcohols, sulfides and thiols – molecules of significantly lower toxicity than the CWA surrogate. Hydrolysis and dehydrohalogenation were the predominant detoxification pathways, via the formation of the intermediate cyclic sulfonium, whether under light or in the dark. Ambient light irradiation promoted the photo-oxidation and photo-degradation by radical intermediates formed. With an unhindered oxygen rich surface, underlying highly polarizable lattice structure, and large accessible surface area, barium titanate nanoparticles are investigated as a potentially useful medium for photoreactive detoxification of chemical warfare agent vapors.

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1. Introduction

Chemical Warfare Agents (CWAs), first deployed during WW I, continue to be a major concern to the modern warfighter and to

civilians under threatening circumstances, despite multilateral treaties in place that ban their use. Therefore, the development of detoxification materials and filters (gas masks, uniforms, etc.) continues to be a necessity. Activated carbons are the most widely used adsorption media in gas masks [1–5]. Recent years research effort have turned towards the development of advanced materials that can act as multifunctional detoxifiers when applied as filters or dispersed on fabrics [6–11]. The desired activity includes simultaneous adsorption, degradation, and detection of CWAs [9]. Various Metal Organic Frameworks and Nanomaterials have been tested in this context and were shown to enhance detoxification capabilities against CWAs [12–15]. However, the majority of these tests were performed in liquid suspensions [9,11,15–17], and not for vapors or aerosols, the states in which CWAs are usually deployed [2,18,19].

Nanoparticles offer a large surface-to-volume ratio and a higher concentration of under-coordinated surface sites than the corresponding bulk. In this work, we introduce the concept of a nanostructured perovskite as a potential detoxifier of CWAs. We hypothesize that properly prepared nanostructured complex oxides can provide new avenues for developing more sophisticated multifunctional materials. Their activity is expected to be governed by transition metal chemistry and strong coupling of organic molecules to an active dipolar surface. The classical perovskite complex oxide barium titanate (BaTiO_3), studied for many years and frequently abbreviated to BTO, is commonly associated with modern electronic components such as multilayer capacitors (MLCCs), non-volatile memory (NVM), and positive temperature coefficient thermistors (PTCR). The broader, related family of complex oxide perovskites are explored for their utility in the emerging fields of multiferroics, magnetoelectrics, energy storage conversion, and sensors [20–23]. Recent work has shown that specifically tailoring perovskite oxides with certain compositions can optimize their performance as catalysts [24]. Since the perovskite oxides represent a very wide range of electronic and electrical behavior as well as a tunable band gap as a function of composition, it is reasonable to suppose that a great deal of untapped potential could be harnessed, through the exploration of novel approaches to a perovskite oxide synthesis and catalyst design at the nanoscale [25,26].

Barium titanate has been explored for potential photocatalytic activity, such as organic pollutant degradation [27,28], including choroorganics [29], and dye decomposition and decolorization [30]. Generally, there is a small number of reports on remediation applications of BaTiO_3 and very few focus on sub-micron systems. For adsorption, catalysis, and preparation of nanostructured BTO with a large internally accessible surface area, it is desirable to synthesize BTO nanocrystals that are relatively monodisperse, uniform in size and with maximization of undercoordinated surface sites. The barium titanate nanoparticles studied here were synthesized using a method known colloquially as self-collection or gel-collection [31,32]. Precursors are mixed in stoichiometric amounts in an organic solvent to yield a gel monolith, which is completely separated from its initial liquid phase. Transformation of the precursors to relatively uniform, monodisperse, 100% crystallized nanocrystals takes place in a non-aqueous polar protic environment, and the absence of ligands enables the system to produce nanocrystals without an abundance of organic content ligating to or adsorbed onto a surface, which could later inhibit catalysis. The surface states of the nanocrystals typically evolve to be short chain groups (hydroxy, ethoxy) in a low density [32].

Remediation of organic compounds that are considered a threat to humans and/or the environment, remains an important challenge for modern society. Numerous studies on the removal of organic pollutants, such as dyes and herbicides, by various materials (MOF, metal oxides/hydroxides, carbons) have been reported [17,33–39], but so far limited attention has been paid to the evaluation of perovskites as potential decontamination media

[24,26,40]. Previously, an aqueous suspension of BaTiO_3 (with particle sizes in a broad range from 85 to 286 nm) was shown to photocatalytically degrade the herbicide diclofop-methyl [41]. The degradation mechanisms involved redox reactions linked to photo-generated free radicals (OH^\cdot , H^\cdot , O_2^\cdot) upon UV-light illumination. Uniformly and regularly spherically shaped BaTiO_3 nanoparticles (55 nm average size) showed adsorption and photocatalytic degradation under UV towards methyl red [42], and micron-scale BaTiO_3 (>100 nm) showed a negligible removal capability of aqueous Rhodamine B (RhB). Thamima et al. showed that sphere shaped barium titanate nanopowders can efficiently degrade various dyes like methylene blue, malachite green and alizarin red S (ARS) under UV light irradiation [43]. Nano-cubic barium titanate photocatalytically degraded crystal violet dye [44]. Moreover, cubic phase BaTiO_3 nanoparticles showed an elevated photocatalytic capability under UV light irradiation for the removal of humic acid [45].

Composites of $\text{BaTiO}_3/\text{Bi}_2\text{O}_3$ were also found to be photoactive against RhB [46]. Annealed BaTiO_3 (1200 °C in air, sizes ~622 nm) led to an improved photo-decolorization and dye removal rate under UV-Vis irradiation [27]. In the absence of irradiation, enhanced adsorption of dye molecules has been attributed to the ferroelectricity of the tetragonal phase enabling a Stern layer, which can lead to a strongly bound layer of the polar dye molecules on the surface, and additionally to an efficient separation of the photoexcited carriers, due to the internal space charge layer [27]. These results suggest that many factors, such as the size of particles, the surface polarization as a result of the ferroelectricity, and the surface chemistry, can play a role in the interactions with BaTiO_3 , and in a potential decontamination of organic compounds on this material or on other similar complex transition metal oxides.

With respect to the interactions of perovskites with CWAs, limited studies have been carried out [40]. On the contrary, TiO_2 (pure or doped with metal) has been extensively studied for detoxification of CWAs, but the processes took place in a liquid phase [47]. Ultrasonically sprayed nanostructured perovskite-type (CdSnO_3) thin films were reported to have a good sensing response to 2-chloroethyl ethyl sulfide (CEES or 2-CEES, $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$) vapors [48]. In addition, barium titanate and strontium titanate ceramic fibers were demonstrated as having high detoxification ability against the simulant of thiophosphonate nerve agent VX, paraoxon, but only in aqueous medium [40].

Here, the use of nanoscale BaTiO_3 is studied against vapors and droplets of 2-chloroethyl ethyl sulfide (CEES), which is a commonly accepted surrogate of the “the King of battle gases” – mustard gas (bis(2-chloroethyl) sulfide, $\text{C}_4\text{H}_8\text{Cl}_2\text{S}$). The vast majority of reported results on CWAs detoxification is carried out on their surrogates, owing to safety regulations in academic institutions. Even though CWAs surrogates are toxic, their toxicity is considerably lesser than those of the chemicals they represent. Our objective is the analysis of this perovskite's catalytic activity. The identification of all formed compounds, volatile or adsorbed on the surface, is used to identify the predominant detoxification pathways, while characterization of the surface of the exhausted nanoparticles helps to determine the role of the surface features. The application of 8–12 nm nanoparticles may open an innovative road for the potential deposition of nanoscaled highly photoactive phases on porous textiles for simultaneous and fast adsorption, degradation, and detection of CWAs [6,9,11,49].

2. Experimental section

2.1. Materials

Barium isopropoxide ($\text{Ba}(\text{O}i\text{Pr})_2$) was purchased from Alfa Aesar (99.5% trace metals basis), titanium isopropoxide ($\text{Ti}(\text{O}i\text{Pr})_4$) was purchased from Sigma-Aldrich (99.999% trace metals basis) and

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