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Air detoxification with nanosize TiO_2 aerosol tested on mice

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ABSTRACT

A method for fast air purification using high concentration aerosol of TiO_2 nanoparticles is evaluated in a model chemical catastrophe involving toxic vapors of diisopropyl fluorophosphate (DFP). Mice are used as human model in a closed 100 dm^3 chamber. Exposure of mice to 37 ppm of DFP vapor for 15 min resulted in acute poisoning. Spraying TiO_2 aerosol in 2 min after the start of exposure to DFP vapors resulted in quick removal of DFP vapors from the chamber's air. Animals did not show signs of poisoning after the decontamination experiment and exposure to TiO_2 aerosol alone. Reactive oxygen species (ROS) and antioxidant activity (AOA) of mice blood plasma were measured for animals exposed to sound of aerosol generator, DFP vapors, TiO_2 aerosol and DFP vapors + TiO_2 aerosol. Reduced ROS and increased AOA were found for mice exposure to sound, DFP and TiO_2 aerosol. Exposure to DFP and decontamination with TiO_2 nanoparticles resulted in decreased AOA in 48 h following the exposure. The results suggest that application of TiO_2 aerosol is a powerful method of air purification from toxic hydrolysable compounds with moderate health aftermaths and requires further study and optimization.

1. Introduction

Development of methods for quick purification of air is important for countering the threats of technogenic and man-caused catastrophes. The speed of air cleaning is critical since it determines time of exposure that determines aftermaths of accidents.

Nanosized high surface area oxide materials of low toxicity such as titanium dioxide provide opportunity of removing toxic contaminants via reactive adsorption and photocatalytic oxidation [1,2]. The studies on interaction of highly toxic materials with nanomaterials are usually performed using less toxic simulants. Dimethyl methylphosphonate (DMMP) [3–5], diisopropyl methylphosphonate [6], trimethyl phosphate, thiethyl phosphate and diethyl phosphoramidate [7] often serve as simulants of organophosphorous nerve agents. DMMP undergoes hydrolysis of one methoxy group upon adsorption over hydroxylated TiO_2 surface with formation of adsorbed methyl methylphosphonic acid and gaseous and adsorbed methanol [3–5]. Photocatalytic oxidation after reactive adsorption results in complete mineralization of the adsorbed organic compounds and accumulation of surface phosphates that cause catalyst deactivation [4,5,8]. Improvement of photodegradation efficiency of organophosphorous compounds over TiO_2 can be obtained by introducing sites with increased binding constants [6].

Diisopropyl fluorophosphate (DFP) is a close toxic simulant for chemical agents sarin and soman (Scheme 1). Previously, adsorption and photocatalytic oxidation of DFP was investigated over rutile polycrystalline film [9]. Adsorption of DFP over TiO_2 is accompanied by hydrolysis of P–F group that determines high DFP toxicity. Thus, partial detoxification is obtained even before complete photocatalytic destruction.

It has been demonstrated that the rate of air purification from DMMP vapors over polycrystalline anatase TiO_2 film is limited by transport of DMMP molecules from gas phase to the film surface [5]. Decreasing the diffusion distance can increase the speed of air purification greatly. Recently we suggested using high density TiO_2 photocatalytic aerosols for fast air purification [10,11]. Characteristic time for DMMP removal was about 0.3–0.7 min that is over one order of magnitude faster than for a polycrystalline film [5]. In the present study, we apply an aerosol technique for air purification from DFP vapors in a model catastrophe involving mice as human simulants.

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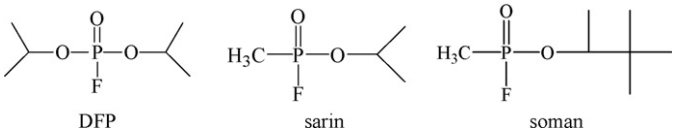

Scheme 1. Structural formula of cholinesterase inhibitors DFP, sarin and soman.

The application of nanomaterials for air treatment in the presence of humans is related with the problem of unknown toxicity effects. Recent studies indicated that TiO_2 nanoparticles possess cytotoxicity for neural cells and fibroblasts [12]. Chronic exposure to high concentrations of TiO_2 can cause cancer in lungs of rats but was not so dangerous to humans, mice and hamsters [13]. This suggests similarity of human and mice response to nanoparticles. TiO_2 aerosol inhalation caused lung inflammation in mice upon exposure over long time [14,15]. The toxic effect was due to the decrease of the alveolar's macrophage ability to clear particles from lungs because of masking macrophage surface with TiO_2 [16,17].

The objective of this work was to estimate the efficiency of TiO_2 aerosol air decontamination from chemical agent surrogate DFP in a simulated catastrophe involving mice as a human model. A very concentrated aerosol of agglomerated TiO_2 primary particles of size ~8 nm and short exposure time of 15 min was found sufficient to purify air from chemical agent surrogate DFP in the presence of mice. Chemical, behavioral and biochemical effects of aerosol generator, TiO_2 aerosol and combined exposure to DFP and TiO_2 aerosol are investigated for mice as model living objects. A very quick detoxification was obtained with TiO_2 aerosol that allowed reducing the model catastrophe aftermaths to a minor health damages.

2. Experimental

2.1. Materials and animals

Diisopropyl fluorophosphate (DFP) was a product of Aldrich. Caution: DFP is a very poisonous compound! All manipulations with DFP should be performed in a fume hood. Wearing protective gloves and goggles is obligatory. Avoid inhalation and skin contact.

TiO_2 Hombikat (100% anatase, primary particles size ~8 nm) was purchased from Sachtleben Chemie GmbH (Germany). Before the aerosol experiments, TiO_2 was dried in a drying oven at 120 °C overnight.

Animals were outbreed white male mice with mass 31–32 g grown at Tomsk State University. All the animals were kept at identical conditions before the experiments.

The source of radicals for antioxidant activity measurements was aqueous fir extract. The quantity of superoxide radicals generated using this source was over 100 times higher than that from standard radical source 1,1-diphenyl-1-picrylhydrazyl [18].

2.2. Experimental setup

The scheme of the experimental setup is depicted in Fig. 1. Exposure of mice to TiO_2 aerosol, chemical agent simulant DFP and detoxification was performed inside a Plexiglas chamber of volume 100 dm^3 (8). A cage (9) for mice was placed on the floor of the chamber. The size of the cage cells was about 1 cm. 20 mice was placed in the cage for performing each experiment. TiO_2 spraying was performed with a sonic aerosol generator (10) described in detail previously [10,11]. 5 g of dried TiO_2 Hombikat was loaded inside the generator before the experiments involving the aerosol spraying. The generator was electrically fed by a power supply (13) with frequency 220 Hz. Injection of liquid CWA simulant DFP was accomplished through the sampling port (11). A hotplate (12) served as evaporator and ensured quick evaporation of the injected simulant.

20 mice were put in the cage, and then the chamber (8) was sealed. The volume of air in the chamber was enough for 20 mice breathing during the typical experiment time of 20 min since the volume of air inhaled by each mouse is about 0.06 ml, frequency of inhalation is 200 min^{-1} that gives an estimate of air used in breathing equal to 4.8 dm^3 [19].

2.3. Analysis

Quantitative determination of air components inside the chamber (8) was done using an IR long path gas cell (3) model G-3-8-H (Infrared Analysis Inc.) connected to the chamber. Air was continuously circulated through the chamber and the IR cell under the action of a Teflon coated membrane pump (1). The flow rate of circulation was approximately 5 dm^3 min^{-1} and allowed obtaining the response time of 18 s. The spectra were taken with an FTIR spectrophotometer Vector-22 (Bruker). Calibration for DFP concentration measurements was performed in the chamber without animals and TiO_2.

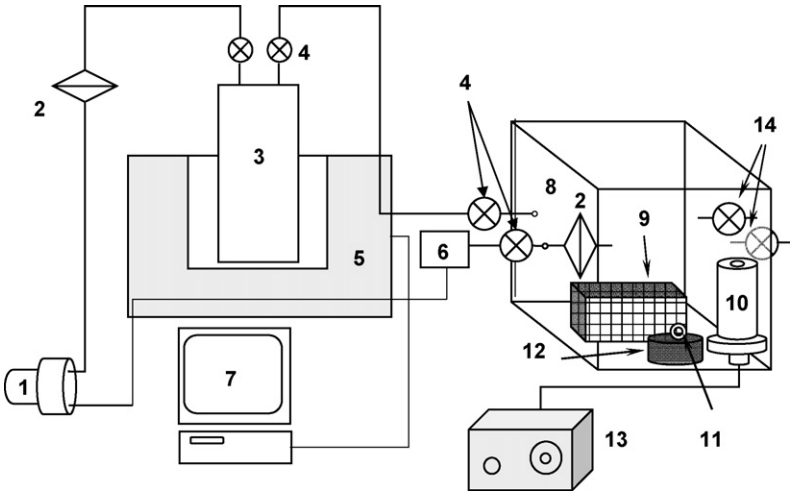

Fig. 1. Experimental setup. (1) Membrane pump, (2) air filter 0.2 μm, (3) long path IR gas cell, (4) stopcocks, (5) FTIR spectrometer Vector 22 (Bruker), (6) temperature and humidity meter, (7) computer, (8) Plexiglas chamber, (9) cage with mice, (10) aerosol generator, (11) sampling port, (12) evaporator, (13) power supply and (14) air purge ports.