



# Sunlight assisted photocatalytic detoxification of sulfur mustard on vanadium ion doped titania nanocatalysts



P.V.R.K. Ramacharyulu<sup>a</sup>, J. Praveen Kumar<sup>a</sup>, G.K. Prasad<sup>a,\*</sup>, B. Singh<sup>a</sup>,  
B. Sreedhar<sup>b</sup>, K. Dwivedi<sup>c</sup>

<sup>a</sup> Defence Research and Development Establishment, Jhansi Road, Gwalior 474002, India

<sup>b</sup> Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500007, India

<sup>c</sup> School of Studies in Chemistry, Jiwaji University, Gwalior 474011, India

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## ABSTRACT

Photocatalytic detoxification of sulfur mustard was studied on vanadium ion doped titania nanocatalysts under the irradiation of sunlight. Data obtained on vanadium ion doped titania nanocatalyst was compared with that of bare and commercial TiO<sub>2</sub> nanocatalysts. Vanadium ion doped titania nanocatalyst was found to be more active than bare and commercial titania nanocatalysts towards the photocatalytic detoxification of sulfur mustard in ecological sunlight irradiation. 100% of sulfur mustard was found to be detoxified within 180 min on vanadium ion doped TiO<sub>2</sub> nanocatalyst. Whereas, it took 240 min for bare TiO<sub>2</sub> and 420 min for commercial TiO<sub>2</sub> nanocatalysts to completely degrade sulfur mustard. Sulfur mustard was found to have degraded to products like acetaldehyde, carbon dioxide, disulfide, sulfoxide and sulfone of sulfur mustard, chloro ethyl vinyl sulfide, chloro ethyl vinyl sulfoxide, etc.

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## 1. Introduction

Cleaning of surfaces tainted with chemical warfare agents (CWAs) is of great concern for emergency responders and related authorities who deal with terrorist attacks and stockpile destruction. Sulfur mustard (HD) (C<sub>4</sub>H<sub>8</sub>SCl<sub>2</sub>, 2,2'-dichloro diethyl sulfide) is a vesicant, alkylates DNA and causes fatality to cells. Detoxification of HD is a difficult process from the mechanism point of view [1].

Photocatalysis has been established as a potential technique for the detoxification of toxic chemicals and it has been playing a promising role in the cleanup of environment [2]. Good chemical stability, less toxicity, high photoactivity and economical viability make TiO<sub>2</sub> a potential candidate for photocatalysis. However, disadvantage with TiO<sub>2</sub> is its large band gap which requires UV-A light (388 nm) to activate it [3,4]. Many methods have been used to widen the spectral response of TiO<sub>2</sub> to improve its photocatalytic activity in visible light. TiO<sub>2</sub> photocatalysts with enhanced visible light activity have been prepared by doping with metals [5–8], non-metals [9–11], sensitizers [12,13], and reduced forms of titania [14]. Enhanced activity under visible light irradiation enables

the doped TiO<sub>2</sub> catalyst to efficiently degrade CWA into non toxic products in ecological sunlight which contains more amount (46%) of visible light in addition to UV-A light (4–5%) [15]. The visible light activity of metal ion doped TiO<sub>2</sub> can be explained by new energy levels introduced in the band gap of TiO<sub>2</sub> by dispersion of metal ions in its matrix. Electrons can be excited from valence band to defect states created below the conduction band of TiO<sub>2</sub> by photon with enough energy. Additional benefit of transition metal ion doping is the improved trapping and enhanced lifetime of charge carriers which inhibit electron–hole recombination during irradiation [8–17]. Decreased charge carrier recombination results in enhanced photoactivity. Besides chemical modification of TiO<sub>2</sub>, enhancement of photoreactivity can be achieved by reducing the particle size to nano dimensions [16,17]. Recently, vanadium ion doping on TiO<sub>2</sub> has been a topic of interest [18–22] because of economical viability, enhanced catalytic activity of V centres of oxide substrates. The ionic radius of vanadium ion (0.58 Å) is similar to that of titanium ion (0.61 Å) because of which vanadium ion can be used as a substituent to titanium ion in its vacant sites.

Photocatalytic oxidation of HD and its simulants has been studied since 1990 over titania catalysts [23–29]. Regarding this, Neatu et al. studied the photocatalytic degradation of HD on M/TiO<sub>2</sub>/SiO<sub>2</sub> catalysts and observed the enhanced activity under visible light irradiation on doped catalysts whereas the bare catalyst showed activity only under UV irradiation [30]. Subsequently, they also

\* Corresponding author. Tel.: +91 751 2390169; fax: +91 751 2341148.  
E-mail address: [gkprasad2001@gmail.com](mailto:gkprasad2001@gmail.com) (G.K. Prasad).

studied Au–TiO<sub>2</sub> catalyst for the detoxification of nerve gases and HD at room temperature upon visible light irradiation [31]. Thereafter, Prasad et al. reported the photocatalytic decomposition of HD on ZnO and TiO<sub>2</sub> nanoparticles. According to their observations, ZnO, TiO<sub>2</sub> nanoparticles have degraded 100% of in 12 h and 4 h, respectively in natural sunlight [32,33]. Naseri et al. studied photolytic and photocatalytic degradation of HD using TiO<sub>2</sub> nanoparticles and polyoxometalates and decontaminated HD completely in 3 h [34]. However, they used only UV irradiation for the same. Application of sunlight and visible light active TiO<sub>2</sub> nanocatalysts as sorbent decontaminant for the detoxification of CWA is interesting as these materials can be sprayed on contaminated surfaces for the cleansing applications. However, to the best of our knowledge there are no reports available in the literature till date on application of vanadium ion doped titania nanocatalyst for the photocatalytic degradation of HD in the presence of sunlight. Inspired by the above studies, we have synthesized vanadium ion doped TiO<sub>2</sub> nanocatalysts, characterized them by X-ray diffraction (XRD), transmission electron microscopy (TEM), nitrogen adsorption (N<sub>2</sub> BET), UV–vis spectroscopy, infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) techniques. Subsequently, we have studied photocatalytic degradation reactions of HD under the irradiation of sunlight by using gas chromatography (GC) and gas chromatography mass spectrometry (GC–MS) techniques.

## 2. Experimental

### 2.1. Materials

Vanadyl acetylacetonate, titanium tetraisopropoxide (TTIP) were procured from Acros organics, UK. Dichloromethane, ethanol, ethyl acetate and acetonitrile were obtained from E. Merck India Ltd. Commercial TiO<sub>2</sub> nanocatalyst (CT) of size (~30 nm) was purchased from Alfa Aesar, UK. HD of 99% purity was synthesized in our establishment. (This is a very toxic agent; hence these experiments should be done under the guidance of trained personnel equipped with individual protective equipment only.)

### 2.2. Preparation of photocatalysts

TiO<sub>2</sub> nanocatalysts were prepared by sol–gel hydrolysis of titanium (IV) isopropoxide (TTIP) followed by hydrothermal treatment. TTIP was dissolved in anhydrous ethanol and the solution was added dropwise to the mixture of distilled water and ethanol under vigorous stirring at room temperature. Obtained precipitate was transferred into a Teflon lined autoclave and heated at 80°C for 24 h. Resultant solid was dried at room temperature and finally labelled as bare TiO<sub>2</sub> nanocatalyst (HT) and washed with excess of ethanol to remove remaining organic moieties [35]. Similarly, metal ion dopant was introduced by adding appropriate amount of vanadyl acetylacetonate into deionised water preceding to the hydrolysis of TTIP. By varying concentration of vanadyl acetylacetonate, different samples were prepared. The samples were labelled as 0.1 VT (0.1 at.% V in TiO<sub>2</sub>), 0.25 VT (0.25 at.% V in TiO<sub>2</sub>), 0.55 VT (0.55 at.% V in TiO<sub>2</sub>), and 2.0 VT (2.0 at.% V in TiO<sub>2</sub>).

### 2.3. Characterization of photocatalysts

XRD data was recorded on X'Pert Pro Diffractometer of M/s Panalytical, Netherlands make using Cu K $\alpha$  radiation. TEM measurements were done on Tecnai transmission electron microscope of FEI make. Samples were suspended in 30 mL of acetone, and the suspension was sonicated for 30 min. Subsequently, suspension was placed on carbon coated copper grids of 3 mm diameter and dried at room temperature prior to the analysis. Nitrogen

adsorption measurements were done on ASAP 2020 surface area analyser of Micrometrics, USA. Reflectance spectra were recorded on Lambda 25 UV–vis spectrophotometer of PerkinElmer make by taking spectralon as internal standard. FT-IR measurements were done on PerkinElmer, USA instrument. XPS data was recorded on KRATOS AXIS 165 instrument. GC of Nucon Engineers, India make equipped with FID detector, BP5 column (30 m length, 0.5 mm i.d.) was used to monitor degradation of HD. GC–MS system (5975 B) of Agilent, USA make was used for quantification and identification of reaction products. Calibrated equipment manufactured by Technovation India Ltd., was used to monitor carbon dioxide (CO<sub>2</sub>) and X-am 7000 detector of M/s. Dräger, Germany make was used for quantitative identification of acetaldehyde.

### 2.4. Photocatalytic degradation

Hundred milligrams of nanocatalyst (VT or HT or CT) was taken in a quartz tube and 100  $\mu$ L of dichloromethane solution containing 2  $\mu$ L of HD was spiked on it. Dichloromethane was allowed to evaporate. Subsequently, quartz tube containing the nanocatalyst was irradiated by sunlight. Intensity of light was measured by digital light metre (SLM 110 model) of A.W. Sperry Instruments, USA with help of adapters provided. Value of irradiance of sunlight was determined to be 95 mW/cm<sup>2</sup>. Experimental setup already reported [32] was used for this work also. All the experiments were carried out at room temperature (30  $\pm$  2°C). The gaseous products formed on surface of catalyst when irradiated with light were trapped by suction through liquid nitrogen trap of 40 mL/min. The trapped solution was analyzed for CO<sub>2</sub> and CH<sub>3</sub>CHO by the equipment discussed in earlier section. Remaining HD was extracted after periodic intervals of time using acetonitrile. The extracted samples were analyzed with GC affixed with FID detector to monitor the amount of degraded HD. Later, the solution was concentrated to 1 mL and analyzed for products by GC–MS. Degradation products which formed in major quantity were quantified by GC–MS (Model 5975B and 6890N).

## 3. Results and discussion

### 3.1. Characterization of photocatalysts

#### 3.1.1. XRD data

Fig. 1 shows the XRD data of synthesized VT and HT nanocatalysts. The data depict peaks at  $2\theta$  values 25.2; 37.8; 48.0; 53.8; and 62.7. These peaks can be attributed to the presence of (1 0 1), (0 0 4), (2 0 0), (1 0 5), and (2 1 5) indices. This XRD pattern illustrates  $2\theta$  values and relative intensities that match with (JCPDS 21–1272) data of anatase phase of TiO<sub>2</sub>. It also illustrates peak broadening indicating the formation of crystallites with size in nano dimensions. No peaks corresponding to oxides of vanadium are observed even for samples doped with 2 at.% of vanadium (2 VT). Apparently, VT nanocatalysts were found to retain the anatase phase with no phase separation leading to rutile titania or vanadia even after doing. This observation also indicates the incorporation of vanadium ion into TiO<sub>2</sub> lattice. Crystallite sizes of VT catalysts were calculated by Scherrer equation and they were found to be 6.12, 6.45, 5.85, and 6.76 nm, respectively for 0.1 VT, 0.25 VT, 0.55 VT and 2 VT nanocatalysts. The crystallite size of HT nanocatalyst was found to be 11 nm.

#### 3.1.2. Electron microscopy data

TEM images of both doped (0.1 VT) and bare (HT) nanocatalysts are shown in Fig. 2(a and b). No significant differences are observed when the images of VT and HT nanocatalysts are compared. TEM images clearly indicate that the particle size is homogeneous and fairly small. It can also be seen from the images that spherically

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