Photoassisted remediation of toxic chemical warfare agents using titania nanomaterials

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This review deals with recent technological advancements in the area of environmental photocatalysis assisted by titania nanomaterials towards the degradation of toxic chemical warfare agents. High surface area, enhanced photoactivity, low toxicity, and high stability make titania nanomaterials potential candidates for application in environmental remediation of toxic chemical warfare agents.

Keywords: Photocatalysis, Environmental pollutants, Nanomaterials, Titania.

Introduction

Remediation of environment polluted with toxic chemical warfare agents (CWA) is a challenging task for authorities who deal with public health and environmental safety. Abnormal health symptoms appear when the human beings are exposed to these hazardous chemicals. Decontamination of surface or environment tainted with these toxic chemicals is the main job we have to do, to avoid health hazards. This can be achieved by application of decontaminants on the surface or environment. Application of nanosized titania photocatalysts as decontaminant is interesting, as powder of the same can be sprayed on contaminated surfaces or added to contaminated environment to assist decontamination by adsorptive removal of toxic chemicals. After adsorption, they participate in photocatalytic reactions and assist decontamination of toxic chemical in the presence of light radiation.

A glance on photocatalysis by TiO₂

In 1972, Fujishima and Honda discovered UV light induced splitting of water on TiO₂ photoanode when it was used in combination with Pt counter electrode in an aqueous electrolytic solution¹. Following this, Frank and Bard studied the degradation of cyanide in water by using TiO₂, thereby opening of a field called environmental photocatalysis². Since then, TiO₂ photocatalysis has attracted significant attention because of its promising applications in environmental remediation and degradation of pollutants. Excitation of TiO₂ with photons of light energy greater than band gap is the primary process underlying its vast area of photochemistry. When a photocatalyst material like TiO₂ is irradiated with light of UV region, whose energy is greater than band gap (3.2 eV), electron–hole pairs are generated. These electron–hole pairs finally lead to the formation of hydroxyl radicals and super oxide anion radicals due to their interaction with water molecules or surface hydroxyl groups and oxygen. These species in turn react with environmental pollutants and facilitate their decontamination. TiO₂ has been used mainly due to its non-toxicity, water insolubility, hydrophilicity, cheap availability, stability against photocorrosion and for its suitable flat band potential which can induce desired redox reactions without biased potential. Furthermore, TiO₂ can be supported on various substrates such as glass, fibers, stainless steel, inorganic materials, and sand and on activated carbon which allows its continuous reuse. However, the large band gap of TiO₂ (~ 3.2 eV for anatase, brookite, ~ 3.0 eV for rutile) requires excitation wave length of UV region. Use of sunlight instead of UV light for photocatalysts, is an economically viable approach for environmental remediation³.

However, sunlight reaching the surface of earth was found to contain only 4–5% of UV light fraction...
which can excite TiO$_2$ and enable it to destroy toxic chemicals. Utilization of sunlight for photocatalytic reactions can be done by tuning the band gap response of titania into the visible region$^3$. Thus, tailoring properties of titania is required to utilize large fraction of sunlight and also to realize the indoor applications of this photocatalyst in the presence of artificial fluorescent light. For this purpose, TiO$_2$ has been modified by various strategies like coupling with narrow band gap semiconductor, metal ion / non metal ion doping, codoping with two or more foreign ions, surface sensitization by organic dyes or metal complexes, surface fluorination and noble metal deposition. These processes exert a substantial influence in modifying the electronic band and surface structure of TiO$_2$ and result in higher quantum efficiency and reaction rates for the degradation of organic pollutants under UV / solar light illumination (Figure 1)$^4$.

Degradation of toxic chemical warfare agents using undoped nano titania and non metal doped nano titania

Fox et al.$^5$ studied photo oxidation of 2-chloroethyl ethyl sulphide (CEES), 2-chloroethyl methyl sulphide in water/acetonitrile mixture and observed a complex mixture of hydrolysis and oxidation products. Vorontsov et al.$^6$-$^10$ studied photocatalytic gas phase oxidation of diethyl sulfide (DES), CEES, and 2-chloro ethyl phenyl sulfide (CEPS) over several types of TiO$_2$ photocatalysts. Products corresponding to C-S bond cleavage and direct oxidation of sulfur or carbon atoms were detected. Carbonate and sulfate species were also detected on TiO$_2$ surface after complete photo oxidation of DES or CEES or CEPS and were found to be responsible for TiO$_2$ deactivation. However, this photocatalyst was completely reactivated by washing with water. Vorontsov et al.$^{10}$, Hirakawa et al.$^{11}$, and Rusu et al.$^{12}$ studied photocatalytic degradation of isopropyl methylphosphonofluoridate and related organo phosphorous compounds on the surface of TiO$_2$. Following this, Prasad et al.$^{13}$ studied photocatalytic degradation of ethyl paraoxon in aqueous solution by using titania nanoparticulate film. They described that the photocatalytic degradation reaction of organo phosphorous compounds begins with destruction of P-O-C bonds. Subsequently, P, C atoms were found to be oxidized gradually, and contribute to photocatalytic degradation of paraoxon. Thereafter, Ramacharyulu et al.$^{14}$ studied the role of particle size of titania on photocatalytic decontamination of sulfur mustard (HD). Decontamination efficiency was found to decrease when particle size was increased from 11 nm to 1000 nm. They also studied sunlight assisted photocatalytic decontamination of HD by using ZnO nanoparticles.$^{15}$ On the other hand, Cojocaru et al.$^{16}$ used TiO$_2$-active carbon & N-TiO$_2$-active carbon composites for studies on photocatalytic degradation of chemical warfare agents soman, VX, and HD. These materials were found to decompose HD, soman and VX in high concentrations. This property seemed to be aroused from the synergism between adsorption on active carbon and visible light promoted photoactivity by modified titania.

Degradation of toxic chemical warfare agents using metal doped nano titania

Doping TiO$_2$ lattice with metal ions introduces new energy levels in the band gap (Fig. 1). Depending on the dopant identity and concentration, the band gap of TiO$_2$ can be tailored to extend the photoresponsiveness into the visible light region. Addition of metal ions to TiO$_2$ can influence the photocatalytic properties leading to creation of new energy states. The metal ions work also as charge carrier traps and effectively enhance the charge separation of electrons and holes resulting in an increase in the quantum yield of surface photoreactions. Doping with transition metal ion increases the formation of Ti$^{3+}$ ions leading to the enhancement in photocatalytic activity. Increased number of Ti$^{3+}$ states might cause more oxygen defects and facilitate the efficient adsorption of
oxygen on titania surface. The formation of O$_2^–$ upon chemisorption of oxygen requires the presence of surface defect sites which could be enhanced by transition metal ion doping. Since the redox energy states of many transition metal ions lie within the band gap of TiO$_2$, substitution of metal ions into TiO$_2$ introduces intra band states close to conduction band (CB) or valence band (VB) edge inducing visible light absorption at sub band gap energies. Consequent red shift in the band gap absorption was attributed to the charge transfer transition between the d electrons of the dopant and CB or VB of TiO$_2$. Obtained materials show enhanced visible light activity for the degradation of toxic chemicals. In this connection, Stengl et al.\textsuperscript{17} studied photo induced degradation of CWA related chemicals such as DMMP and CEES on Zr doped anatase TiO$_2$ nanoparticles. They have also showed that, particle size played an important role in the properties of nanocrystalline TiO$_2$ for degradation of CWA. The presence of Zr$^{4+}$ dopant, increased the surface area, crystallites size and accelerated the surface hydroxylation. Complete degradation of soman or VX on Zr-doped titania was found to be achieved in 1 minute for sample with $\sim$13.2 weight % Zr. Besides this, Stengl et al.\textsuperscript{18} studied degradation of HD on zirconium doped Ti–Fe oxides and explored Fe–Ti–Zr oxides as better reactive sorbents for the fastest removal of HD from a non-polar solution. Basic functional groups and their reactive sites were found to assist faster degradation of HD. The specific surface area values of most of the sorbents tested were found to be sufficient to achieve nearly complete (~99 percent) removal of sulphur mustard within several hours at 1/50 mass ratio to the sorbents. Stengl et al. also prepared nano dispersed titanium (IV)–manganese(IV) oxides by homogeneous hydrolysis of titanium oxo-sulphate and potassium permanganate with 2-chloroacetamide. According to them, prepared Ti(IV)–Mn(IV) oxides were found to exhibit 95.2% – 89.3% of decontamination efficiencies against CWA. Neatu et al.\textsuperscript{21} studied photo-degradation of HD over V, Fe and Mn-doped titania–silica photocatalysts under UV light radiation. Photocatalytic tests confirmed the promoter role played by the dopant ions. In the presence of doped photocatalysts, the decomposition rate was found to be higher than on the parent titania–silica catalyst. Water adsorption on the external surface of the photocatalysts also played a major role in this reaction. The product distribution suggested two main pathways of the degradation. They were oxidation of sulfur, carbon atoms and the cleavage of the C–S bond. The products of the complete oxidation (SO$_2$ and CO$_2$) were detected in very small quantities. Neatu et al.\textsuperscript{22} also studied detoxification of CWA using titania supported gold nanoparticles. This photocatalyst completely detoxified different CWAs and exhibited exception stability and recyclability. Panayotov et al.\textsuperscript{23} studied photo oxidation of a HD gas simulant over TiO$_2$-SiO$_2$ mixed oxide photocatalysts using transmission IR spectroscopy. Photo oxidation of 2-CEES at 200 K resulted in the formation of adsorbed CO$_2$ product (2355 cm$^{-1}$) as well as other partially oxidized products exhibiting carbonyl stretching modes at 1709 and 1560 cm$^{-1}$. The partially oxidized products blocked readsorption of 2-CEES by Si-OH groups on the used photocatalyst. The CO$_2$ product could be desorbed by heating to about 300 K. Reactivation by heating to 400 K restored the ability of TiO$_2$-SiO$_2$ photocatalyst to fully adsorb 2-CEES. The reactivated material exhibited an ability to continuously photo oxidize 2-CEES.

Degradation of pollutants using nano titania modified by sensitizers

Cojocaru et al.\textsuperscript{24} studied decomposition of a CWA, HD using photocatalysts prepared by doping with sensitizers on various supports (Fig. 2). A series of heterogeneous photocatalysts consisting of metal phthalocyanine or 2,4,6-triphenylpyrylium were prepared by supporting them on zeolite Y, MCM-41, silica, titania-silica. They were tested for the photocatalytic decomposition of HD. These tests demonstrated that, iron and manganese phthalocyanine

![Fig. 2 – Mechanism of photocatalytic degradation of toxic chemicals on sensitizer modified TiO$_2$.](image-url)
and 2,4,6-triphenylpyrylium embedded in NaY or titania-silica matrix were found to be suitable for the degradation of HD using UV and visible irradiation.

**Mechanism of photocatalysis**

Vorontsov *et al.*^8^ studied the mechanism of photocatalytic oxidation of CEES, a simulant of CWA. Photocatalytic oxidation of above organic sulfide started with sulfur radical cations. Further, the radical cation of sulfur compound had undergone reaction with oxygen or superoxide ions to form sulfone, which was converted to sulfoxide via a reaction with another CEES molecule. The radical cation was also found to undergo cleavage of either of C–S bonds. The alkyl cations have reacted with water to produce the corresponding alcohols, ethanol and 2-chloroethanol. 2-Chloroethanol was found to be detected in the extracts from the TiO$_2$ surface. Another transformation route of alkyl radical cations was proton elimination. The proton elimination was found to produce ethylene and chloroethylene. The thyl radicals CH$_3$CH$_2$S• and •SCH$_2$CH$_2$Cl recombined in all possible combinations giving the detected products diethyl disulfide, 2-chloroethyl ethyl disulfide, and bis (2-chloroethyl) disulfide. The disulfides in turn interacted with photogenerated holes and underwent reactions similar to CEES radical cations. The corresponding radicals CH$_3$CH$_2$SS• and •SSCH$_2$CH$_2$Cl were found to recombine with each other and formed tetrasulfides and trisulfides. Acetaldehyde and chloroacetaldehyde were found to be formed due to oxidation of ethanol and chloroethanol respectively. Higher selectivity was demonstrated for the oxidation of alcohols to aldehydes. It was indicated that the mechanism (Fig. 3) was highly cross-linked and various stages can follow in complex combinations^9^.

**Future Directions**

Enhanced photocatalytic activity, less toxicity, economical viability of titania nanomaterials promise revolutionary applications in the area of environmental remediation of toxic chemicals, self-cleaning tiles, cementous materials, self-cleaning windows, etc. The photocatalytic oxidation of organic compounds in both aqueous and non aqueous environment has received a large amount attention, additionally there is a rapidly increasing focus on the oxidation of inorganic compounds in the gas phase such as NO$_x$, SO$_x$, etc. Photocatalytic reduction of organic compounds, metal containing ions, and studies on disinfection of bacteria by illuminated titanium dioxide have also received increasing attention. Their versatility and tailored properties make them budding sorbent materials also for futuristic CBW decontamination applications.

**References**


