Interactions and Reactions of Guest Molecules with Nanotubular Materials

Titania nanotubes were produced in large quantities using hydrothermal synthesis. Short titania nanotubes and nanosheets were also produced based on various processing techniques. Based on systematic structural modeling we demonstrated that the structure of titania nanotubes is based on delaminated anatase along the [001] direction. For the first time, the x-ray diffraction pattern of titania nanotubes is successfully explained. This provides the basis for understanding the properties of decontamination of chemical warfare agents (CWAs). The anatase-like (001)
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List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)


Number of Papers published in peer-reviewed journals: 8.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations


Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Number of Manuscripts: 0.00

Patents Submitted

Patents Awarded

Graduate Students

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### Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

- The number of undergraduates funded by this agreement who graduated during this period: 0.00
- The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields: 0.00
- The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields: 0.00
- Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): 0.00
- Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering: 0.00
- The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense: 0.00
- The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

### Names of Personnel receiving masters degrees

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### Sub Contractors (DD882)
Titania nanotube is a new form of titania with unique morphology and local structures. It is an efficient porous sorbent material for a wide variety of organic molecules and exhibits unusually high decontamination efficiency for many chemical warfare agents (CWAs) including VX. Significant progress has been made in understanding the basic structure of titania nanotubes. This structure offers the largest surface area achievable of any TiO₂ structure with all Ti and O atoms exposed to relatively small guest organic molecules. This is a very desirable property for molecular absorption and catalytic reactions with guest molecules. What are the reaction mechanisms of CWAs with titania nanotubes? How could the reaction rates be improved? Answers to these questions require much detailed information on local structures and surface functional groups of titania nanotubes and related materials and significant progress has been made in this program in this area. Systematic study of local structures and properties of titania nanotubes under various synthesis and processing conditions has been carried out. A variety of techniques were employed for structural characterization such as microscopy, XRD, Raman, and NMR. NMR has been employed to study the details of important reaction processes such as dissociative and nondissociative surface hydration processes and reaction processes with CWAs and their simulants. To complement the experimental work, theoretical modeling of structures and reactions has also been pursued. These studies should have major impact on the development of decontaminants and self-decontaminating coating materials. This comprehensive study sheds light on the basic physical and chemical processes related to the interactions of CWA-related organic molecules with the nanoporous materials of titania nanotubes and derivatives. The close collaboration between UNC-Chapel Hill and U.S. Army Edgewood Chemical Biological Center ensured that the basic research carried out has had direct impact on the practical development in the area of CWA decontamination and mitigation.

Titania is a material of great interest due to its many unique properties, including catalytic and photoelectrochemical applications. Like most catalysts, the surface area and surface chemistry of titania are two of the most important factors that determine its properties. Neither would reach its maximum efficiency through the use of titania nanocrystals. In contrast, multilayered titania nanotubes are shown to achieve both the largest surface area and the unique surface chemistry to obtain the highest efficiency for certain chemical reactions including the decontamination of chemical warfare agents such as VX. Titania nanotube is a new form of titania. Figure 1 shows TEM and SEM images of titania nanotubes at various length scales. The TEM image in Fig. 1 (a) reveals the multilayered tubular structure with inner diameters of 5-6 nm, outer diameters of 10-12 nm, and interlayer spacing of 8.7Å. The model of such multilayered titania nanotube is shown in Fig. 1 (b). The SEM images in Fig. 1 (c) and (d) show how a typical particulate of aggregated micron-long titania nanotubes form into porous clusters. The aggregation of such tubular objects with high aspect ratios leads to particulates that are very
porous, preserving the intrinsically large surface area of titania nanotubes. This is in contrast to
the aggregation of nanocrystals which pack densely and eliminate the effective surface sites
necessary for chemical reactions. As we found out through our study, titania nanotubes are air
stable for maintaining chemical reactivity. In our studies we made breakthroughs in
understanding the basic structure of titania nanotubes and we demonstrated the extraordinary
performance of titania nanotubes in decontaminating the CWA VX achieving a rate comparable
to liquid decontaminants.

**Titania Nanotubes** There are two basic questions that are important for the development
of nanostructured titania for catalytic applications. (1) What is the largest surface area achievable
for TiO$_2$ without losing the characteristics of bulk TiO$_2$? (2) Does the surface area originate from
the desired titania surface? It is particularly important to increase the surface area of surfaces
with desirable properties. Theoretical and experimental evidences indicate that anatase (001)
surface performs better for various chemical reactions. However, due to its large surface energy,
the (001) surface is the minority surface in typical anatase nanocrystals. Here we explain the
structure of multilayered titania nanotubes that have the highest achievable area of titania-like
surface. Furthermore, the surface is exclusively anatase (001)-like.

The structure of anatase TiO$_2$, as shown in Fig. 2 (a), is traditionally viewed as three-
dimensional, in which the lengths of its apical bonds, all along [001], are longer than the
equatorial bonds. This anisotropy could lead to delamination (such as by intercalation of Na$^+$
ions) along the [001] direction as illustrated in Fig. 2 (b). The multilayered delaminated anatase
sheets could bend and roll up, as illustrated in Fig. 2 (c), into the nanotubular structure shown in
Fig. 2 (d), analogously to graphene sheets and multi-walled carbon nanotubes.

![Figure 2: (a) Anatase unit cell. (b) Delaminated anatase with interlayer spacing of 8.7Å. (c) Rolling of
the delaminated anatase layers. (d) Formation of multilayered titania nanotube. (e) a. Experimentally collected XRD of
titania nanotubes. b. Simulated XRD pattern of nanotubes rolled around the delaminated anatase [010] axis. c. Simulated XRD of nanotubes rolled around the delaminated anatase [100] axis. d. Simulated XRD of nanoscrolls,
each formed by rolling up a single sheet. e. Simulated XRD pattern of delaminated anatase sheets.](image)

We can synthesize this structure through a hydrothermal process as described later in
detail in Task 1. This layered delaminated anatase structure possesses the highest possible
surface area (including the intercalated space), 400 m$^2$/g, without losing the basic TiO$_2$
characteristics. Furthermore, because the direction of delamination occurs exclusively along the
[001] direction, the surface is all anatase (001)-like; all Ti atoms are undercoordinated (fivefold
rather than sixfold coordinated) and half of the O atoms are bridging oxygens (rather than
threecold coordinated as in bulk anatase (Fig. 2 (b))).

A series of our experiments and computer modeling fully established the basic structure
of titania nanotubes. The structure of delaminated anatase sheets (Fig. 1 (b)) provides the
foundation for the structure of titania nanotubes. Figure 2 (e,a) shows the experimental x-ray
diffraction (XRD) pattern of titania nanotubes. The simulated XRD pattern of delaminated
anatase sheets, shown in Fig. 2 (e,e), recreates all peaks observed in the actual experimental XRD (Fig. 2 (e,a)) along with other peaks that are not observed experimentally. The 10° peak corresponds to the interlayer distance. The creation of a true multilayered titania nanotube model is quite challenging unlike multilayered carbon nanotubes. After constructing various nanotubular and nanoscrolls models we now understand the basic structure of the nanotubes. Figure 2 (e,b) shows the simulated XRD pattern of nanotubes by rolling the double layers of delaminated anatase around the [010] axis. The experimental XRD matches the model excellently, including many detailed features. In contrast, Fig. 2 (e,c) shows the simulated XRD pattern of nanotubes formed by rolling the double layers of delaminated anatase around the [100] axis, this does not match satisfactorily with the experimental XRD. Figure 2 (e,d) shows the simulated XRD pattern of nanoscrolls by rolling a single layer of delaminated anatase. Again, the match with the experimental XRD is far from satisfactory due to the incorrect atomic registry along the [010] axis. The structure of titania nanotubes is highly ordered and the atomic registry between layers along the tube axis is preserved whereas it is lost along the circumference of the tube. This is fully expected since preserving the atomic registry between the layers along the circumference requires unrealistically highly strains bonds.

Although we do understand the basic structure of titania nanotubes at the level of XRD, properties such as structural relaxation and surface functionalization of titania nanotubes are far from obvious from XRD studies. Such structural information is important for understanding the surface chemistry. Raman, NMR and FTIR spectroscopy techniques have been used along with computational methods to assist the understanding of reaction processes in multilayered titania nanotubes.

Decontamination of CWA VX One of the known problems in the detoxification of VX by base-catalyzed hydrolysis in aqueous solution is the production of the stable toxic product S-(2-diisopropylaminoethyl) methylphosphonothioic acid (EA-2192). There is a significant benefit to employing solid oxide sorbents as VX decontaminant as due to the reaction selectivity no EA-2192 is produced [13-15]. Figure 3 (a) shows the 31P NMR magic-angle-spinning (MAS) spectra of 5 wt% VX in AP-Al2O3 taken after a reaction time of 24 hours and 15 days, respectively. (b) 31P NMR MAS spectra of 5 wt% VX added to titania nanotubes taken after 12 and 57 minutes, respectively, after VX addition. (c) The proposed reaction scheme of hydrolysis.
diffusion resulting from a high native viscosity and low vapor pressure. The $^{31}$P MAS spectra in Fig. 3 (b) clearly shows that the reaction rate is much faster with titania nanotubes than with AP-Al$_2$O$_3$ (disappears after 1 hour rather than a month). The very sharp $^{31}$P peaks in Fig. 3 (b) indicates that VX and the reaction product EMPA are quite mobile and are not bound to the surface. This supports the idea that the role of titania nanotubes in this reaction is catalytic in nature.

As described by the reaction scheme shown in Fig. 3 (c), water molecules are involved in the reaction process, the behavior of water on titania surface is also a topic of our investigation. Unlike on other surfaces, water is predicted to adsorb dissociatively on anatase (001) surface (Fig. 4). In titania nanotubes the Ti-O bonds are strained due to curvatures (Fig. 4(a) and 4(b)) and the effect of water dissociation is an important issue. We have investigated in detail water dissociation and reactions of small molecules with titania nanotubes by $^1$H NMR. A comprehensive approach is used employing structural computation, XRD, Raman spectroscopy, and NMR. A computational approach at the DFT level (Gaussian, CASTEP, VASP) and force field level are proven to be very useful for studying structure and reaction processes as illustrated in Fig. 4 (c) and (d). Since titania nanotube is multilayered, it is important to know whether guest molecules can intercalate between the inner-layers of the nanotube (Fig. 4 (e)).

Our study shows that titania nanotubes are very efficient for CWA decontamination as shown in the table in Figure 5 below. It is clear that hydration has a huge effect on the half-life of CWAs. It is also very interesting to note that water improves the VX decontamination rate in titania nanotubes whereas it slows down the rate in anatase nanocrystals. In our studies we observed a gradual $^{31}$P peak shift toward low field as the reaction time increased. This may be related to gradually increased intercalation. The vastly improved reaction rate in titania nanotubes is believed to be due to subtle placement of water molecules, self-catalyzed reaction via EMPA which is not chemically bound on surface as in Al$_2$O$_3$, large surface area, and accessibility.
In summary, we have demonstrated that titania nanotubes are very efficient for the decontamination of CWAs, especially VX. The detailed structures and surface chemistry are investigated by various analytical techniques such as NMR. It is shown that the surface of titania nanotubes are anatase (001) surface. The structure is based on delaminated anatase along the [001] direction. Different processing techniques have been applied to titania nanotubes to produce new structures such as titania nanosheets and to modify the surface chemistry. This study demonstrates that titania nanotubes can be developed into a very promising and practical product as decontaminant for chemical warfare agents.

Figure 5: Table of half-life time of HD, GD, and VX in various decontaminants. An example of $^{31}$P MAS NMR spectra of VX on titania nanotubes is shown along with the proposed reaction scheme.