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(4)

AGENT DEGRADATION VIA CATALYTIC AND PHOTOCATALYTIC REACTIONS ON SURFACES AND IN ORGANIZED ASSEMBLIES

Sixth Interim Report

by

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Introduction

Research pursued under Contract no. DAJA45-87-C-005 has concentrated on the catalytic and photocatalytic destruction of simulants for V-agents in oxide semiconductor systems, in particular titanium dioxide. Near UV irradiation of TiO_2 semiconductor particles suspended in solution generates electrons and holes in the conduction and valence bands, respectively, free charge carriers that are highly reactive reductants and oxidants. We have previously shown that all the simulants employed underwent complete oxidation and mineralization in the presence of light activated TiO_2. In addition, surface adsorbed hydroxide and peroxide ions act as powerful nucleophiles promoting ester hydrolysis. In view of these very promising results during the last six months we have carried out more detailed investigations to scrutinize the pathway of decomposition of active phosphates on the semiconductor surface. In particular, we have initiated electrochemical and photoelectrochemical investigations with TiO_2 films that are distinguished by a specific fractal-like surface texture resulting in a high roughness factor leading to a large capacity for uptake of chemical agents.

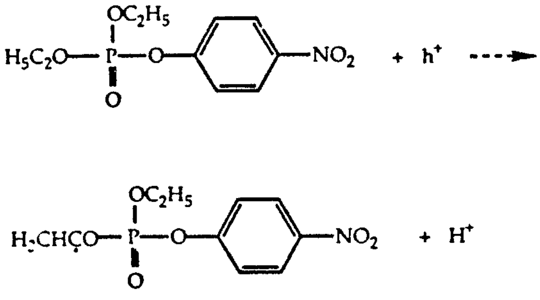
Results

Electrochemical and Photoelectrochemical Investigations of Agent Decomposition on TiO_2 Films:

These films were formed by a sol-gel type procedure yielding layers with a specific surface texture and a high porosity, the roughness factor being 100 to 200. Hydrolysis and oxidative decontamination were tested with agents deposited on the surface which, due to the fractal-type pore geometry, shows a very high capacity for uptake of adsorbent. The decomposition of adsorbed agent was examined both with the film in the dry state and in contact with electrolyte.

Electrochemical and photoelectrochemical techniques were applied in order to analyze the accelerated decomposition of agents on the surface of TiO_2 films. The films were deposited on a conducting substrate and used as a working electrode in a conventional electrochemical cell. The destruction of the agent by valence band holes manifests itself by an enhancement of the anodic photocurrent. This is shown in Figure 1. Here the photocurrent observed under illumination with 380 nm light is plotted as a function of applied potential. It is evident that in the region where the TiO_2 potential is close to flat band conditions, the anodic photocurrent is markedly enhanced when the film is coated with active phosphate ester

This shows that the valence band holes produced by light in the TiO_2 films can directly attack the adsorbed phosphate ester. Presumably, in the case of 4-NPDEP the hole reaction leads to abstraction of a hydrogen atom from the α-CH_2 group, i.e.



(1)

The hydrogen abstraction destabilizes the ester bond which is readily cleaved by water yielding phosphate and the $HO\text{-}\underset{\bullet}{C}H\text{-}CH_3$ radical. In the presence of O_2 the latter is oxidized to acetaldehyde and, ultimately, carbon dioxide. Further kinetic analysis of this interesting heterogeneous charge transfer process is presently being carried out.

We have previously observed that oxygen plays a key role in the photo-catalyzed decomposition of threat agents on TiO_2 surfaces. The role of O_2 is to scavenge conduction band electrons formed concomitantly with the valence band holes by light excitation of TiO_2. In colloidal or powder suspension the valence and conduction band processes always occur simultaneously and therefore cannot be separately investigated. In contrast, the TiO_2 films allow separation of electron and hole transfer processes. The electron reaction was studied in the dark by measuring cathodic currents from the reduction of O_2 using TiO_2 films deposited on a rotating disc electrode. Results are shown in Fig. 2. The cathodic current is plotted as a function of regular frequency for two potentials, i.e. -0.375 and -0.45 V (SCE). The data are plotted according to the Levich equation. From the slope of the straight lines one obtains the number of electrons (n), transferred to O_2 at the electrode surface. Interestingly, n increases from 1 to 4 as the potential decreases from -0.375 to -0.45 V indicating that the reaction mechanism changes from a one-electron reduction:

$$e^-_{cb}(TiO_2) + O_2 \longrightarrow O_2^- \qquad (2)$$

to a four electron process:

$$4e^-_{cb} + O_2 + 4H^+ \longrightarrow 2H_2O \qquad (3)$$

over a relatively narrow potential range. These results are very valuable in view of the important role of O_2^- and peroxides in the nucleophilic and oxidative degradation of threat agents at the TiO_2 surfaces.

Future Pursuits

We plan to extend these electrochemical and photochemical investigations to VX simulants and vesicants such as CEES. In the latter case, it is of interest to examine, apart from oxidative decomposition, an alternative route of detoxification

$$Cl\text{-}CH_2CH_2\text{-}S\text{-}CH_2\,CH_3 + e^-_{cb} + H^+ \rightarrow Cl^- + CH_3\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_3 \qquad (4)$$

where e^-_{cb} stands for a conduction band electron in the oxide semiconductor. Reaction (4) will again be studied separately in the dark by using the fractal-like TiO_2 films as a cathode in an electrochemical cell.

It is likewise planned to study agent degradation in dispersions of TiO_2 in mixtures of water with organic solvents, e.g. chlorinated alkanes, and in pure organic liquids. The advantage of these systems with respect to pure water is that both solubility of the agent and oxygen is increased which should promote the degradation process.

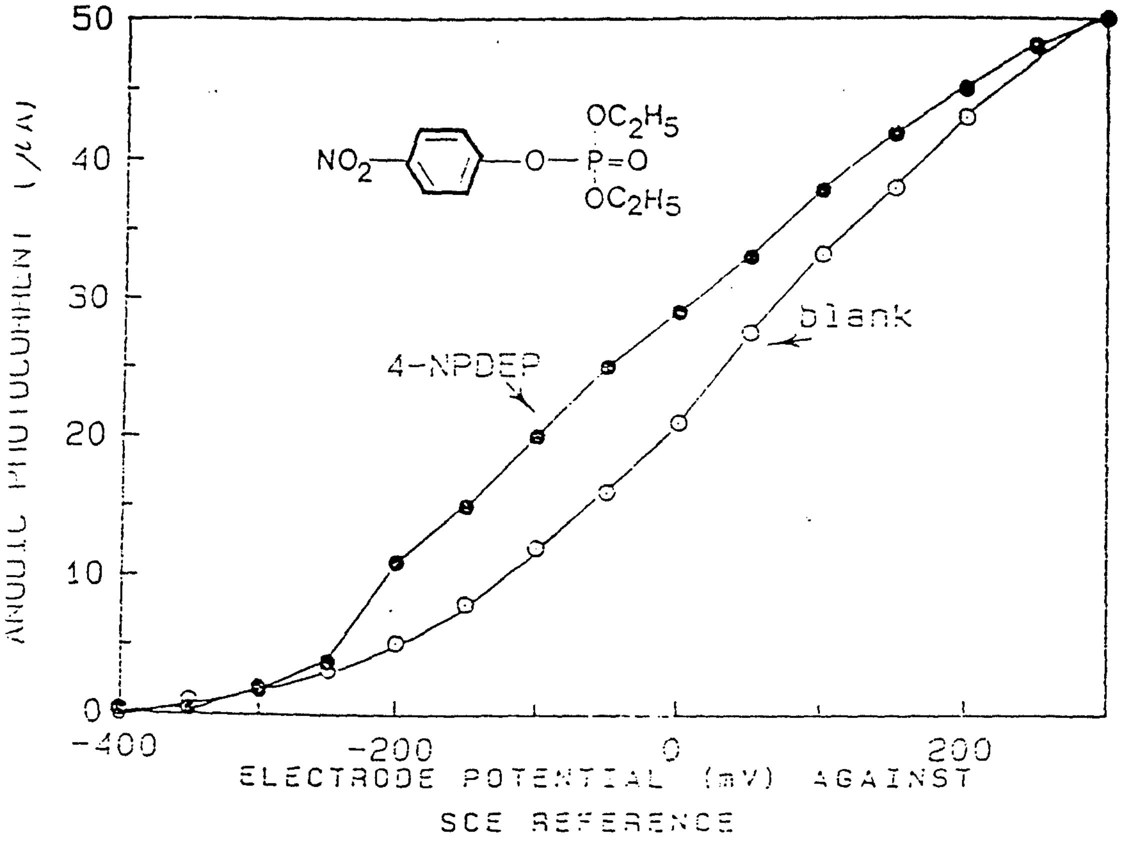
It is proposed to employ promoters in conjunction with oxide semiconductor catalysts to enhance the decomposition of these same threat agents via surface catalysis or photocatalysis. More specifically, we envisage the use of dopants such as Nb^{5+}, Li^+ or Fe^{3+} and oxidation catalysts such as $CaMnO_3$ or CeO_3 as promoters. TiO_2 powders and films with a vanadyl monolayer coating could also be synthesized and the unique properties of these species exploited to increase surface catalysed agent degradation.

A very promising alternative oxidant which will be tested for agent decomposition in solution and on surfaces is peroxooxalate. It is proposed to explore the decomposition of the threat agent by peroxooxalate in solution and on surfaces. Apart from the direct reaction we plan to explore the possibility of electronically exciting the TiO_2 via peroxooxalate decomposition. That would induce formation of electron-hole pairs and rapid degradation of the threat agents even in the absence of light.

Since most of the threat agents are poorly soluble in water simple aqueous dispersions are not suitable for decontamination. Therefore, we plan to employ a surfactant or microemulsion assembly for solubilization together with the catalyst. Apart from conventional surfactants, we plan to include fluorinated surfactants, e.g. perfluorinated carboxylic and sulfonic acids, in our investigations. The advantage of these types of solubilizing agents lies in their chemical inertness and high oxygen retaining capacity which should have a favorable influence on the effectiveness of oxidative degradation processes.

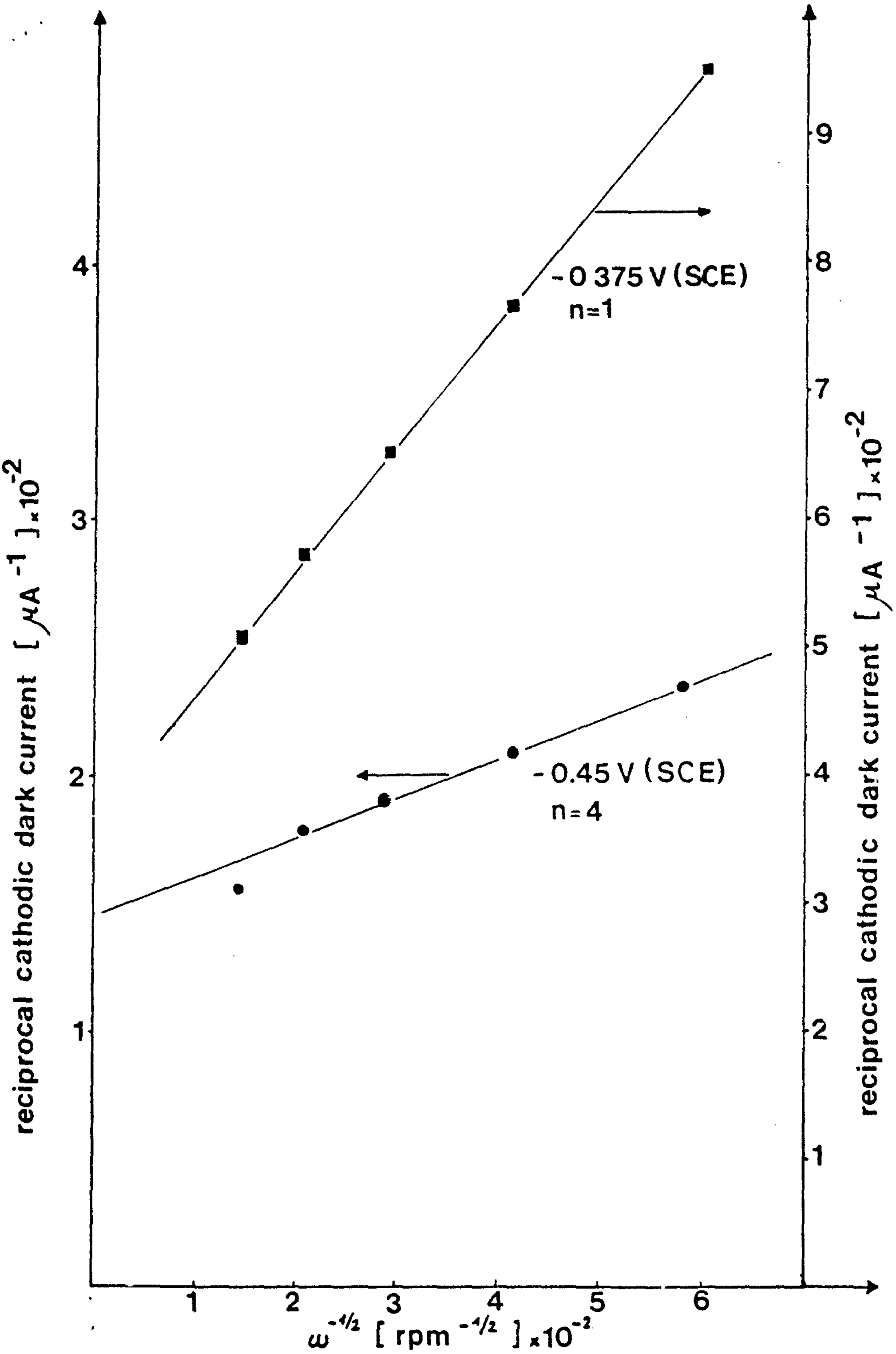
We plan to perform exploratory studies on the destruction of vesicants by transition metal sulfides. Materials such as Co_9S_8 and MoS_2 are commercially employed as hydrodesulfurization catalysts. We also plan to assess whether or not the desulfurization of vesicants can be achieved at room temperature using highly dispersed sulfide catalysts. Investigations will focus on colloidal systems.

FIGURE 1



Photoelectrochemical investigations of TiO_2 films loaded with simulant. The anodic photocurrent resulting from the reaction of the simulant with valence band holes is plotted as a function of applied potential.

FIGURE 2



reciprocal cathodic dark current [μA^{-1}]×10^{-2}
1
2
3
4
-0 375 V (SCE)
n=1
-0.45 V (SCE)
n=4
1
2
3
4
5
6
7
8
9
reciprocal cathodic dark current [μA^{-1}]×10^{-2}
1
2
3
4
5
6
ω$^{-1/2}$ [rpm$^{-1/2}$]×10^{-2}