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Form Approved
OMB No. 0704-0188

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1. REPORT DATE DEC 2008	2. REPORT TYPE N/A	3. DATES COVERED -	
4. TITLE AND SUBTITLE Electro-Optically Pumped Catalytic Coatings For Hydrolysis And Sensing		5a. CONTRACT NUMBER	
		5b. GRANT NUMBER	
		5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)		5d. PROJECT NUMBER	
		5e. TASK NUMBER	
		5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U. S. Army Engineer Research and Development Center; 2902 Newmark Drive; Champaign, IL 61821		8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)	
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited			
13. SUPPLEMENTARY NOTES See also ADM002187. Proceedings of the Army Science Conference (26th) Held in Orlando, Florida on 1-4 December 2008, The original document contains color images.			
14. ABSTRACT			
15. SUBJECT TERMS			
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified	UU
			18. NUMBER OF PAGES 3
			19a. NAME OF RESPONSIBLE PERSON

ELECTRO-OPTICALLY PUMPED CATALYTIC COATINGS FOR HYDROLYSIS AND SENSING

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ABSTRACT

Construction materials have, historically, not been capable of protecting users from toxic contaminants. For example, pipe materials sorb waterborne toxic contaminants, including chemical and biological (CB), toxic industrial chemicals (TICs) and toxic industrial materials (TIMs). Some of these are sorbed quite aggressively. When contaminants are sorbed on pipe materials, the water distribution system becomes contaminated and unusable for long periods of time (Ginsberg and Hock, 2004). We describe self-cleaning coatings and how these can be used inside water-distribution pipes. The coatings can be restored periodically by exposure to energy from optical, chemical, or electrical sources. This periodic treatment also restores the coating to its initial physical characteristics. In particular, we discuss a mixed oxide photocatalyst coating that can induce hydrolysis reactions between water and adsorbed contaminants, and shed adsorbed contaminants when exposed to blue light.

1. INTRODUCTION

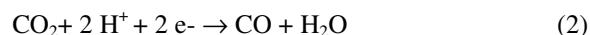
The objective of this work is to provide a potential methodology to rapidly decontaminate a distribution system and restore a safe water supply. Simply coating the pipes to resist sorption can cause long-term problems due to passivation. Non-sorbing materials can be obtained by manipulating properties such as: surface charge, hydrophobicity and acidity. The underlying problem with this approach is that all aqueous environments, including potable water, are full of constituents with dual character (called “bifunctional”), such as having end groups with one being hydrophilic and the other hydrophobic, or one group that is basic (proton accepting) and the other acidic, or with polyionic groups that are cationic and anionic. There are large amounts of natural organic matter with amine, hydroxyl, and carbonylic acid groups which will react with any opposite moiety on the material. The net result is that over time, no matter what properties the material has initially, the properties change towards a more neutral value, until all surfaces reach an intermediate value. Eventually the material becomes coated with carbonaceous compounds and biofilms that readily allow both adsorption and absorption. The only known way to mitigate this natural fouling of all coating systems is to

mechanically, electrically, optically, or chemically clean the surface.

2. CURRENT RESEARCH

We are investigating a bio-inspired approach to cleaning and restoring water distribution pipes *in-situ* using a device that crawls through the system and illuminates a photon-activated cleaning capability embedded in the surface coating. If a distribution system material has the desired hydrophobic, negatively charged, dense properties to prevent large-scale adsorption by a number of potential contaminants, and it can be cleaned when illuminated, then low-cost lighting crawlers can keep the water distribution system in like-new condition and safe. If the photon-activated self-cleaning material can reduce and oxidize a large class of contaminants, then the system could also be restored quickly after an attack. It would have the additional benefit of keeping the system free of biofilms, which can harbor dangerous pathogens, thus mitigating biological attacks.

There have recently been a number of developments in nanostructured materials indicating that one can develop a blue-light-activated “self-cleaning” coating, thus providing a cost-effective solution to keeping a distribution system clean (Hoffmann, 1995). We are working toward developing a material or system of materials that can simultaneously reduce and oxidize a wide range of contaminants when activated with light. Two energetic photoreactions that can occur in water and would clean almost all hydrocarbons from the system are:



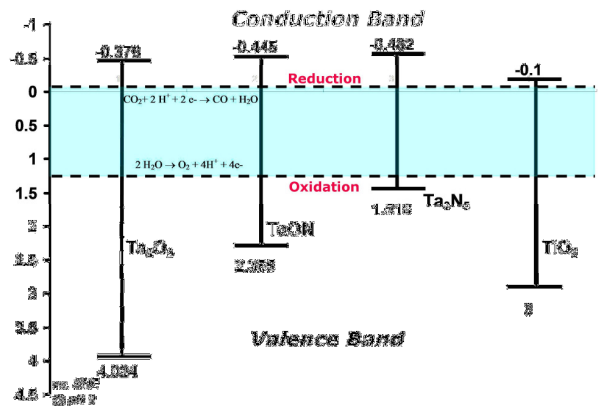


Figure 1. Conduction and valence band positions for TiO_2 , Ta oxides and oxynitrides as compared to the redox potentials for reactions (1) and (2).

For these to occur, the conduction band for any suitable photocatalyst has to be more negative than the 0 eV required for CO_2 reduction and the valence band has to be more positive than the 1.2 eV required for water oxidation.

Therefore, four properties of the material must be optimized simultaneously (Bard et al., 1993):

1. The size of the band gap must be small enough that it can be excited by a low power light source.
2. The placement of the valence band must be negative enough that the reduction rate is rapid.
3. The placement of the valence band must be positive enough that the oxidation rate is rapid. (Figure 1). As is customary, the scale is upside down so that the conduction band appears above the valence band.) (Ginsberg and Hock, 2004).
4. The electron-hole pairs (or *excitons*) in the material must be stable enough that they have time to induce a redox reaction.

Optimization 1: Although it is known that ultraviolet (UV) light alone can drive redox reactions (with no assistance from catalytic materials), these sources are notoriously inefficient as their power input is thousands of times larger than the light output. Hence, the material system must be developed so that a wide range of redox reactions are excited with more efficient blue light, and so that the reaction rate per photon that strikes the pipe wall is high. For example, although titanium dioxide (TiO_2) is an accepted photocatalyst for reducing and oxidizing hydrocarbons in water, its band gap of ~ 3.2 eV requires a high-energy UV light.

Optimization 2: Figure 1 shows the absolute potentials of the reactions and measured conduction and valence band potentials for different high-band-gap semiconductors. While all the materials shown can, in principle, photoca-

lyze the CO_2 reduction, neither TiO_2 nor Ta_3N_5 can do so rapidly enough. TiO_2 possesses a very small overpotential for the reduction step and Ta_3N_5 possesses a very small overpotential for oxidation. Nitrogen-doped tantalum oxide (TaON) reduces the band gap *without* changing the conduction potential. In fact, the addition of nitrogen makes the potential more negative, which acts to increase the kinetics.

Optimization 3: By the Marcus theory (Marcus, 1965), both the relative *and* the absolute values of the electron-hole pair must be greater than the energy required for the redox reaction; the rate is exponentially faster as the difference grows larger. In other words, the conduction band must be well above the reduction line and the valence band must be well below the oxidation line in Figure 1. Recently, work has been done to reduce the band gap in TiO_2 by doping with nitrogen and/or metal co-dopants. The net result is that the band gap was reduced. While this is helpful in allowing use of an inexpensive and efficient blue light, unfortunately for TiO_2 this redshifting only affects the valence band. Because nitrogen doping does not move the conduction band, the overall kinetics are not increased.

Optimization 4: When the electron-hole pair recombines, the exciton driving the reaction is lost. Nanoscale patterning of material can have a huge effect on reaction rates. As the particle size of the photocatalyst becomes smaller, the probability increases that an exciton can reach the material surface before recombination occurs. However, the probability of photon absorption that creates the exciton also decreases, so a tradeoff occurs. Hence, optimization of particle size is an important research question for any particular photocatalyst and targeted reactant. Embedding photocatalysts on oxides such as silica (SiO_2), as shown in Figure 2, has been shown to increase the overall rates of reactions, although the reason for this is still not well understood.

By applying band and band gap engineering techniques both the conduction band and valence band energies of Ta_2O_5 on SiO_2 can be adjusted. Doping the Ta_2O_5 to form TaO_xN_y can also adjust the band gap to the blue light (~ 400 nm) regime. Mixed oxides not only change the conduction band position favorably and decrease the recombination rate, but can also potentially lower cost by using an inexpensive SiO_2 nanoparticle substrate. Due to the interfacial bonding formed when TiO_2 or Ta_2O_5 is supported on SiO_2 , there is a negative shift in the conduction band of the photocatalyst, leading to faster kinetics; this is shown in Figure 3 for a model contaminant, methylene blue, for which the reaction rate increases by a factor of 3.5 at $\sim 50\%$ silica.

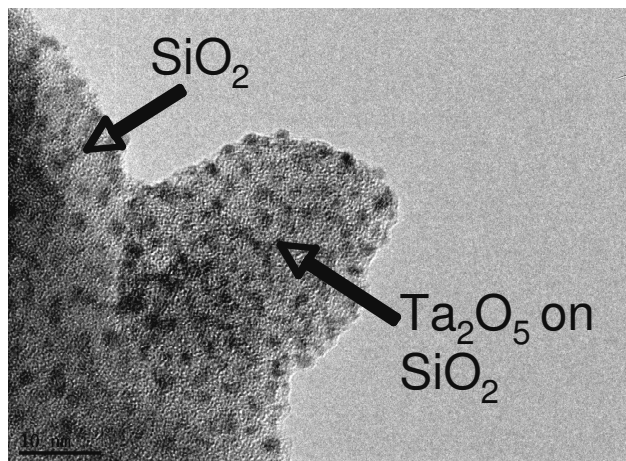


Figure 2. TEM photograph of mixed oxide photocatalysts we have developed with 2 nm nanoparticles of Ta₂O₅ on 20 nm silica particles. The mixed oxides have a slower hole-pair recombination, increasing the probability of redox reactions occurring, increasing kinetics.

Also, given the higher surface area offered by SiO₂, such a supported photocatalyst can provide higher total rates. With these material coating advances, a new system for decontaminating water pipes can be created.

A potential advantage of this type of coating is indicated by how the graph given in Figure 3 changes when a different contaminant is undergoing degradation. This shape change is due to the carbon bond strength of the contaminant being catalyzed. An example of this is given in Figure 4. Here we show reaction rate as a function of SiO₂ percentage with methanol as a contaminant. The change in response shape from Figure 3 to Figure 4 shows that these semiconductor coatings also have the capability to yield information about the type of contaminant present.

3. CONCLUSIONS

Using a water distribution system as an example, we have summarized the properties required for a coating capable of degrading and shedding a wide range of toxic contaminants. In particular: 1) All coatings of this type undergo a process of passivation, therefore they must be actively cleaned, at least periodically. 2) Optical catalytic coatings require the use of nanoparticle-based semiconductors so that cleaning can be achieved with energy-efficient blue light. 3) The band-gap energy of these coatings must span both the oxidation and reduction energies to degrade contamination. 4) The conduction band energy level is determined by the semiconductor used, where the valence band energy is adjusted by doping. 5) There is an optimal semiconductor nano-particle size that maximizes the rate of self-cleaning.

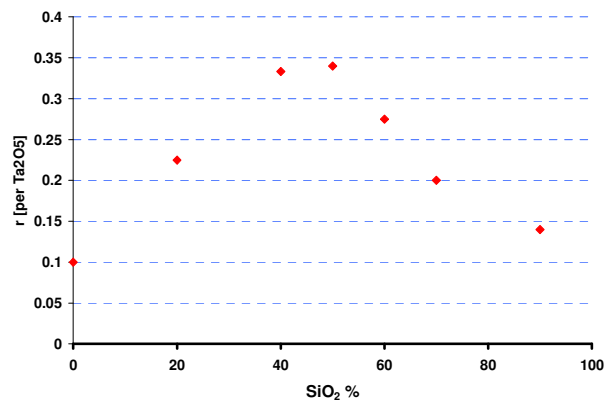


Figure 3. Reaction rate of decomposition of methylene blue on Ta₂O₅ on SiO₂.

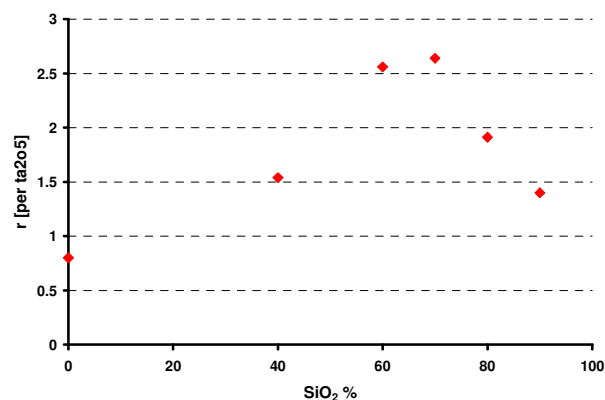


Figure 4. Reaction rate of decomposition of methanol on Ta₂O₅ on SiO₂.

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