ANL/ES/CP-97012

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Presented at

The Third International Conference on TiO_2 Photocatalytic Purification and Treatment of Water and Air

Held

September 23-26, 1997

Radisson Twin Towers Hotel
Orlando, Florida

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ABSTRACT

Titanium dioxide (TiO_2) colloidal particles (~45Å) whose surfaces were modified with chelating agents for photocatalytic removal of heavy-metal ions and their subsequent reduction to metallic form were investigated. Experiments were performed on nanoparticle TiO_2 colloids derivatized with bidentate and tridentate ligands (thiolactic acid [TLA], cysteine, and alanine [ALA]) in batch mode in a photoreactor with 254nm light. We used catalysts designed and synthesized for selective and efficient removal of Pb and Cu with and without added hole scavenger (methanol). Parallel experiments also have been carried out in the dark to study metal ion adsorption properties. Solutions have been filtered to remove TiO_2 and metal particulates. Both the native solution and the metal deposited on the nanocrystalline TiO_2 particles were analyzed. Results demonstrate that for the case of lead, the most effective TiO_2 surface modifier was TLA (>99% Pb(II) removed from solution). Experiments performed to study Cu removal using TiO_2 colloids modified with alanine showed that copper ions were effectively removed and reduced to metallic form in the presence of methanol.

INTRODUCTION

As industrial and municipal wastewater discharge standards become increasingly stringent, there is new impetus for investigating alternative wastewater treatment processes. Wastewaters from many industrial processes, for example metal plating and finishing processes, contain a variety of chemicals such as alkaline and acid cleaners, electrocleaners, and pickling solutions (Wang, L. K. and M. H. S. Wang, 1992). These solutions often are laden with metal ions and rarely can be treated biologically. Conventional physical/chemical wastewater treatment technologies for metal removal used industrially, such as hydroxide or sulfide precipitation, evaporation, and ion exchange, are effective for most wastes but result in hazardous waste sludges requiring costly disposal.

Semiconductor materials such as TiO_2 have proven to be excellent light harvesting materials and mediators in the photochemical degradation of several environmental contaminants. Although photocatalytic degradation can be conducted with several semiconductors, e.g. zinc oxide and cadmium sulfide, TiO_2 has been shown to be the most efficient catalyst (Barbeni et al. 1985; Pelizzetti et al. 1988). Of the three crystal structures (rutile, anatase, and brookite) anatase has been observed to provide the most active photocatalyst. TiO_2-assisted photocatalysis has been studied extensively as a means of the destruction of organic pollutants in solution using photocatalytic oxidation (Ollis and Al-Ekabi 1993; Hoffmann et al. 1995), and to a lesser extent as a way to photoreduce and recover heavy metals (Domenech and Andres 1987; Prairie et al. 1992). TiO_2-assisted photoreduction of certain heavy metal ions such as mercury, gold, platinum, rhodium, chromium, and silver results in the formation of elemental metals (Serpone 1994; Borgarello et al., 1986; Foster et al., 1993). It has been shown recently (Rajh et al. 1996a) that modifying the surface of TiO_2 colloidal particles with certain chelating agents enables photocatalytic reduction of metal ions, such as lead and cadmium, which could not be reduced by unmodified TiO_2.

In this work we investigate removal and reduction of lead and copper ions from aqueous solutions using appropriately derivatized TiO_2 colloidal nanoparticles with and without the hole scavenger methanol.

EXPERIMENTAL

Nanoparticles of titanium dioxide were prepared using the controlled hydrolysis of titanium tetrachloride ($TiCl_4$). $TiCl_4$ was added dropwise to distilled, deionized water at a constant rate, and the solution was dialyzed to remove excess hydrogen and chloride ions. The average particle diameter was 45Å as determined by transmission electron microscopy using a procedure described previously (Rajh, et al., 1996a). Colloid surface modification was achieved by stoichiometrically mixing an appropriate chelating agent -- TLA, cysteine, or ALA (all Aldrich, reagent grade) -- with the nanoparticles for approximately one hour, resulting in thermodynamically favorable adsorption and covalent bonding of the chelating agents to the TiO_2 surface (Rajh, et al., 1996a).

A stock solution of unmodified or surface-modified TiO_2 was pipetted into a 500mL flask and appropriately diluted with distilled, deionized water. Solutions were mixed, poured into quartz flasks, and incubated aerobically or anoxically inside a dark photochemical chamber. Aerobic systems were continuously mixed and purged with air for an hour, while anoxic systems were mixed and purged with nitrogen gas (AGA, >99.995% purity) for at least two hours. Both aerobic and anoxic systems were kept at a pH of 3.

Solutions of metal ions and hole scavengers (methanol) were injected into the TiO_2 suspension. Lead perchlorate stock solution (Aldrich) was the source of metal in all lead adsorption and reduction experiments, while copper sulfate (Aldrich) was the source of copper ions. Suspensions were equilibrated in the dark for 10 minutes. Following equilibration, adsorption reactions were continued in the dark, while photochemical reactions were conducted under illumination from a Rayonet photochemical reactor equipped with eight 254nm mercury lights. At different time intervals samples were collected with a syringe and filtered. Filtrates were analyzed by atomic absorption spectroscopy (Buck Scientific 200A) for residual metal concentrations. Residual precipitates collected on filter papers were investigated with EXAFS (extended X-ray absorption fine structure) and XANES (X-ray absorption near-edge structure) to determine bond distances and oxidation states of metals, respectively (Rajh, et al., 1997).

RESULTS AND DISCUSSION

As described previously (Rajh, et al., 1996 a, b, 1997), modification of the TiO_2 nanoparticle surface with chelating agents such as cysteine (CYS), thiolactic acid (TLA), and alanine (ALA) extends the accessibility of photocatalytic reduction to a wider variety of redox couples. The results of the lead and copper adsorption and reduction experiments are presented below.

I. PHOTOCATALYTIC REDUCTION OF LEAD ON NANOSIZED TITANIUM DIOXIDE

Three types of colloid were used in the experiment: (1) unmodified TiO_2 (2) TiO_2 modified with cysteine, and (3) TiO_2 modified with thiolactic acid. The experiments were conducted aerobically both in the dark and under illumination by the 254nm light. Figures 1 and 2 show the results of these experiments (Skubal and Meshkov, 1996).

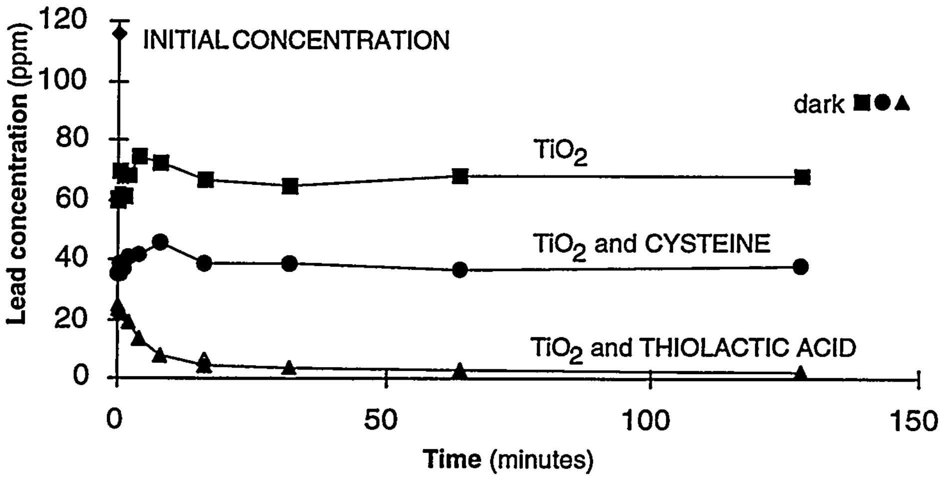

Figure 1. Residual concentration of lead in filtrate as a function of time. Time measurement (time=0) begins after the 10-minute equilibration period in the dark. Initial concentrations are: lead, 115.80ppm; TiO_2, $5.00x10^{-3}M$; CYS, $3.0x10^{-3}M$; TLA, $3.0x10^{-3}M$.

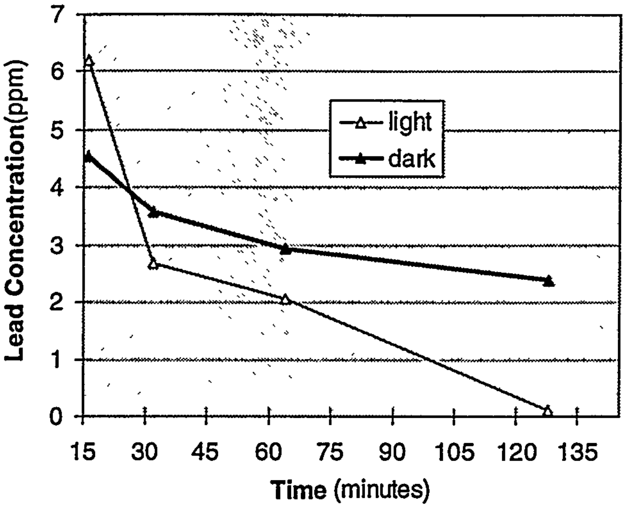

Figure 2. Residual lead concentration during the final 100 minutes of lead/TLA/TiO_2 reactions with and without illumination.

As shown in Figure 1, thiolactic acid-modified titanium dioxide is most effective for removing lead ions from solution. After ten minutes of dark equilibration, TLA-modified titanium dioxide reduced the lead concentration from approximately 115ppm to 20ppm, while unmodified TiO_2 and cysteine-modified TiO_2 reduced it to approximately 40ppm and 60ppm, respectively. After exposure to light, TLA-modified TiO_2 continued to remove lead ions, whereas the unmodified and cysteine-modified TiO_2 did not. Figure 2 shows the last 100 minutes of TLA-TiO_2 reactions. Lead adsorption continued in dark reactions, resulting in a residual lead filtrate concentration of approximately 3ppm Pb after 128 minutes. Illumination greatly enhanced lead removal resulting in a final filtrate concentration of less than 0.10ppm lead after 128 minutes, a removal rate thirty times greater than adsorption processes alone. This enhancement indicates a photocatalytic process: as adsorption of lead ions on the photocatalyst surface increases their proximity to the photogenerated electrons, the likelihood of lead ion reduction also increases. As adsorbed lead ions are reduced, new adsorption sites become available, promoting further lead ion adsorption and reduction. The reduction of lead by TLA-modified TiO_2 is suggested by the color change in filter papers containing the colloid-lead residue, as shown in Figure 3.

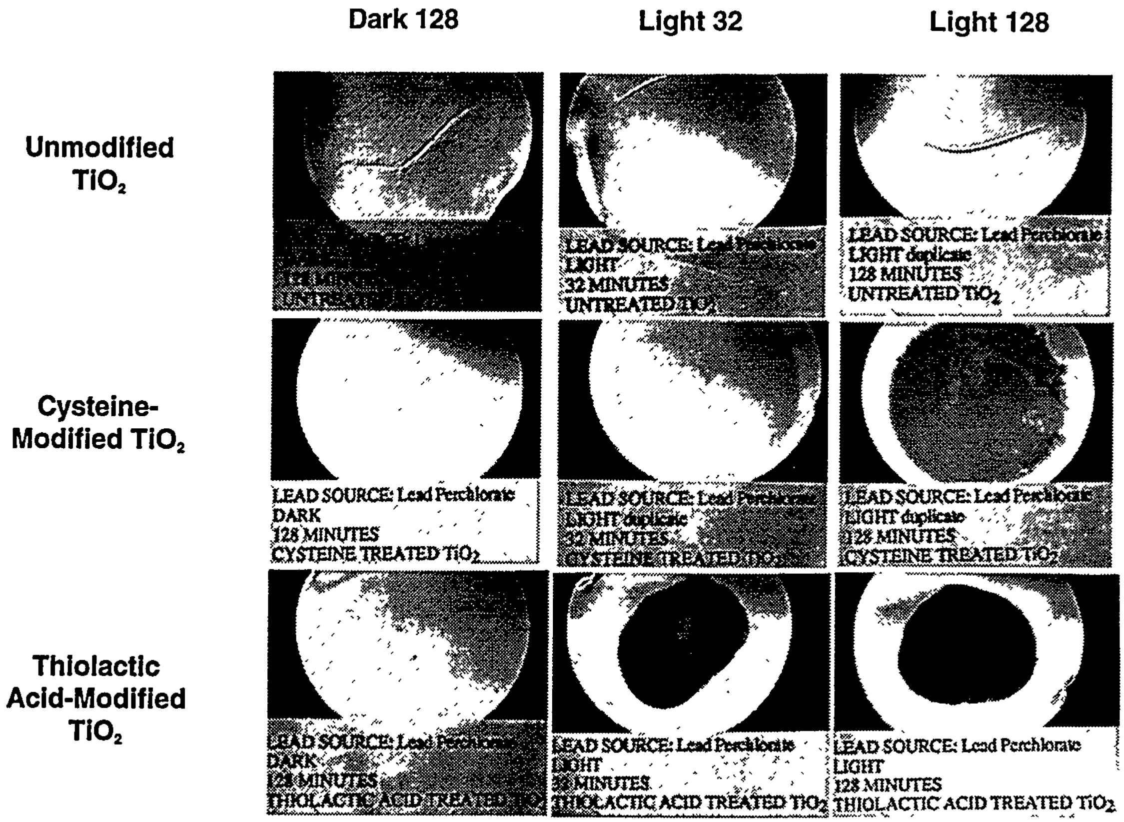

Figure 3. Photographs of filter papers containing residues of lead and unmodified, CYS-modified, and TLA-modified TiO_2 (Skubal and Meshkov, 1996). Samples were kept in complete darkness for 128 minutes or illuminated for 32 or 128 minutes.

As Figure 3 reveals, there is no change in the color of the residual precipitate in all the dark experiments -- unmodified-TiO_2 cysteine-modified TiO_2, and thiolactic-acid-modified TiO_2 (first column) -- suggesting that no reduction of lead ions occurred. Illumination of the unmodified TiO_2 solution also leaves the color of the residue unchanged. However, after 32 and 128 minutes of illumination, the colloids filtered from the cysteine-modified TiO_2 system were deeper in color than their dark reaction counterparts. The most dramatic change in the color of residual precipitate was evident in TLA-modified TiO_2 systems. After 32 and 128 minutes of illumination, TLA-modified TiO_2 lead residue was deep gray and grayish-black, respectively. EXAFS studies suggest that after illumination reduced lead on TLA-modified nanoparticles may be in the form of both elemental lead and lead sulfide formed by reduction of TLA itself (Chen et al., 1998). The only other possible black precipitate, lead oxide, was ruled out because our precipitate could be oxidized further by addition of hydrogen peroxide. Oxidation would not be attainable using this method on lead oxide because lead in this compound already is in the highest oxidation state. The formation of lead sulfide suggests that TLA was oxidatively degraded.

Since the redox potential of unmodified TiO_2 is not sufficiently negative to reduce lead ions, the mechanism of the photocatalytic reduction of lead ions must be explained. The valence and conduction bands of unmodified TiO_2 lie at 2.973eV and -0.227eV vs. normal hydrogen electrode (NHE), respectively at a pH of 3. These values are obtained from the equation for the flat band potential (V_{fb} in eV) of TiO_2 given below (Micic et al., 1995).

$$V_{fb} = -0.05 + (-0.059)pH$$

Upon TiO_2 modification, the flat band potential shifts toward more negative values (Rajh et al., 1996a) as shown in Figure 4. At the same time, complexation of the lead ions with the electron-donating ligand TLA results in modification of the lead reduction potential from -0.126eV to -0.470eV vs. NHE (Figure 4). The increase of the cathodic potential of lead is apparently less than the TiO_2 flat band potential shift as the reduction of lead ions is observed.

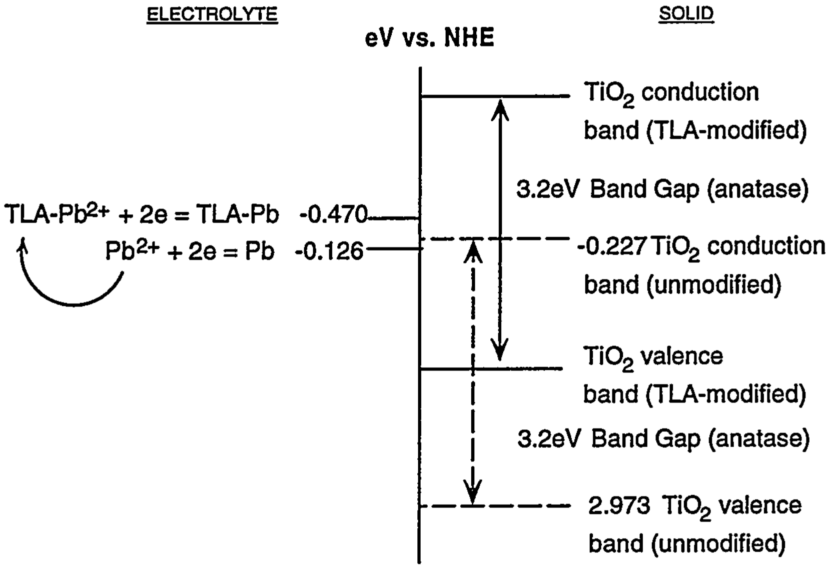

Figure 4. Shift of TiO_2 valence and conduction bands and lead redox potentials after modification with TLA at pH=3.

II. PHOTOCATALYTIC REDUCTION OF COPPER ON NANOSIZED TITANIUM DIOXIDE

Adsorption and reduction of copper was examined using unmodified TiO_2, alanine-modified TiO_2, and alanine-modified TiO_2 with methanol added as a hole scavenger. All copper experiments were performed anoxically to prevent the formation of copper oxides. Figure 5 shows the residual copper concentrations in the filtrate as a function of time in the dark and under illumination.

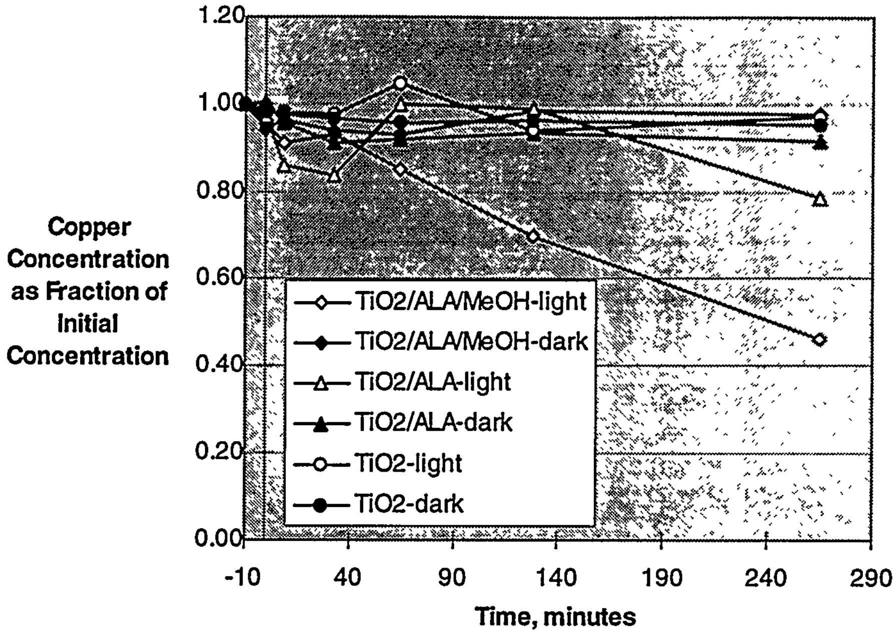

Figure 5. Residual copper concentration in filtrates as a function of time. Initial concentrations: [Cu]=100ppm; [TiO_2]=5.00x10^{-3}M; [ALA]=3.00x10^{-3}M; and [methanol]=0.494M.

Under our experimental conditions at very low copper concentrations, little adsorption occurred during the ten minute equilibration period for all reactions. In the dark no further adsorption occurred throughout the duration of the experiment. For unmodified TiO_2, illumination did not produce a significant decrease in the residual copper concentration. Alanine-modified TiO_2 decreased copper concentration in solution from approximately 100ppm to 79ppm after 265 minutes of illumination. Furthermore, the color of the illuminated ALA-modified TiO_2 solution was light brown, indicating the presence of reduced copper. EXAFS studies confirmed that the brown color was due to elemental copper on the modified TiO_2 particles (Rajh, et al., 1997). Addition of methanol increased the effectiveness of copper removal with alanine-modified TiO_2 in the presence of 254nm light. Figure 5 shows that the initial copper concentration was reduced by more than half during 265 minutes of illumination. The color of the residual precipitate was that of elemental copper; EXAFS studies confirmed that copper ions were reduced to elemental copper (Rajh et. al. 1997).

Figure 6 shows the reduction potential of copper ions relative to the unmodified TiO_2 valence and conduction bands. Although the Cu^{++}/Cu^{0} redox potential is more positive than the conduction band, unmodified TiO_2 does not provide an adequate pathway for electrons to reach the copper ions in the solution.

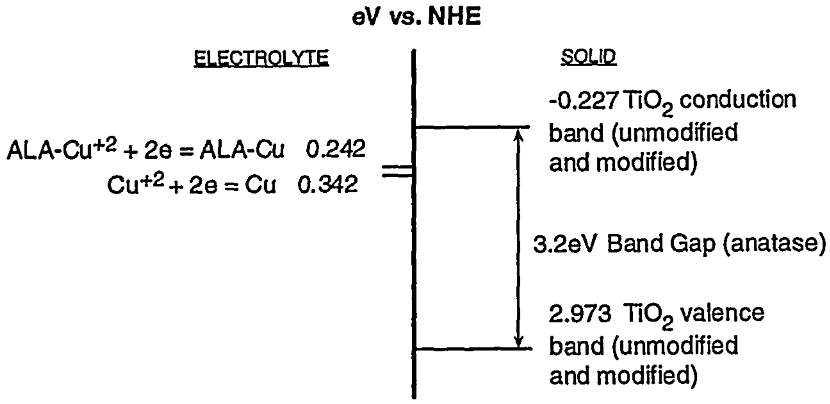

Figure 6. Redox potential of copper and bandgap of TiO_2 after modification with alanine.

As Figure 6 shows, modification of the surface of TiO_2 with alanine does not change the position of the TiO_2 valence and conduction bands, as it did when thiolactic acid was used as a modifier. Once copper is sorbed to alanine, the reduction potential of copper is decreased. However, infrared spectroscopy results suggest that the carboxyl groups from two alanine molecules chelate copper ions while covalently binding to the TiO_2 surface (Rajh and Nedeljkovic, this volume). This structure provides a physical pathway that allows charge transfer to occur. Electron paramagnetic resonance (EPR) studies provided an explanation for the adsorption and reduction properties of ALA-modified TiO_2 with methanol in solution (Rajh and Nedeljkovic, this volume). Methanol greatly promotes the reduction of copper ions on the alanine-modified TiO_2 by acting as an electron donor, and essentially, as a current doubling agent (Rajh et al., 1996a). Through enhanced adsorption, a change in reduction potential, and a current doubling mechanism, copper is effectively photoreduced from a divalent ion to elemental copper in the presence of alanine and methanol.

A possible explanation of why the shift in the band potential is observed for TLA and not ALA is as follows. TLA is bound to the TiO_2 surface bidentally (through the carboxyl and mercapto groups) whereas ALA is bound to TiO_2 through one functional group (the carboxyl group). A bidental binding configuration creates a large dipole moment in the TLA molecule while the dipole moment of ALA is unaffected by surface attachment.

CONCLUSIONS

Experimental work investigating surface modified TiO_2 for the effectiveness of metal photoreduction has shown that modifiers 1) enhance the adsorption of metal ions to the TiO_2 surface, 2) shift the position of TiO_2 valence and conduction bands and/or the reduction potential of the metal ion, 3) increase the separation of electrons, and 4) reduce metal ions to elemental metallic particles. Results of experiments with lead and copper support these conclusions and suggest that the use of surface-modified TiO_2 nanoparticles may provide an innovative way to remove and possibly recover heavy or toxic metals from waste streams. This technology may provide a means to decontaminate wastewaters that cannot be treated by conventional means.

ACKNOWLEDGEMENTS

We gratefully acknowledge support from the Office of Computational and Technology Research, Division of Advanced Energy Projects and Technology Research, U.S. Department of Energy, under contract W-31-109-ENG-38.

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