Implications of Mercury Interactions With Band-Gap Semiconductor Oxides
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Abstract

Titanium dioxide is a well known photo-oxidation catalyst. It will oxidize mercury in the presence of ultraviolet light from the sun and oxygen and/or moisture to form mercuric oxide. Several companies manufacture self-cleaning windows. These windows have a transparent coating of titanium dioxide. The titanium dioxide is capable of destroying organic contaminants in air in the presence of ultraviolet light from the sun, thereby keeping the windows clean. The commercially available self-cleaning windows were used to sequester mercury from oxygen-nitrogen mixtures.

Samples of the self-cleaning glass were placed into specially designed photo-reactors in order to study the removal of elemental mercury from oxygen-nitrogen mixtures closely resembling air. The possibility of removing mercury from ambient air with a self-cleaning glass apparatus is examined. The intensity of 365-nm ultraviolet light was similar to the natural intensity from sunlight in the Pittsburgh region. Passive removal of mercury from the air may be less costly than point source clean-up at combustion facilities.

There are several common band-gap semiconductor oxide photocatalysts. Sunlight (both the ultraviolet and visible light components) and band-gap semiconductor particles can impact the global cycle of mercury in the environment. The potential environmental consequences of mercury interactions with band-gap semiconductor oxides are discussed. Heterogeneous photooxidation might impact the global transport of elemental mercury emanating from flue gases.

Introduction

Mercury is typically present in air at extraordinarily low concentrations of around 1 part per trillion by volume [1-15]. Mercury can exist in air in the elemental, oxidized, and particulate-bound forms. Between 97-99% of the mercury in air is believed to be in the elemental form [1-15]. Oxidized forms of mercury in the atmosphere are believed to include mercuric chloride and mercuric oxide [1-15]. The element and many of its compounds are powerful neurotoxins [16].

Mercury is a semi-noble metal, with a standard electrode potential for oxidation similar to palladium. This relative inertness allows elemental mercury emissions, once in the atmosphere, to transport across the globe. Elemental mercury is slowly oxidized in the atmosphere by ozone and hydroxyl radicals [8]. The low concentrations of elemental mercury, ozone, and hydroxyl radicals contribute to the long residence time of elemental mercury in the air. Elemental mercury in the atmosphere has an estimated lifetime of approximately one year [8]. Elemental mercury is insoluble in water, whereas oxidized forms of mercury are typically much more soluble. Oxidized mercury is scrubbed from the atmosphere by precipitation and deposits in bodies of water. In oceans, lakes, rivers, streams, ponds, bogs, and marshes, oxidized mercury can be methylated by bacteria, plankton, and algae, thereby entering the food chain. Mercury can accumulate at the top of the food chain in large predator fish such as tuna, sword fish, and sharks. Consumption of certain species of fish has been of concern for pregnant women and young children. Numerous fish advisories have been recently posted in the United States [17].

Point source removal of mercury from coal-burning power plants is a difficult endeavor [16,18-23]. Mercury is present in flue gas at low concentrations of around 1 part per billion by volume [16]. The composition of a typical flue gas is given in Table 1. The use of activated carbon sorbent has been the most extensively examined method for removal of mercury from flue gas. There are many deficiencies in the use of activated carbon for mercury capture from power plant flue gas [16,18,19,21,23]. Carbon is a general adsorbent; it will adsorb many of the components of flue gas to some extent, with some in competition with mercury. Carbon sorbents work best at low temperatures. The final state of mercury on the spent carbon sorbent is a concern for the ultimate disposal or use of fly ash. Injection of activated carbon into the duct work of a power plant upstream of an electrostatic precipitator results in poor contact between the sorbent and flue gas. As a result of the poor contacting methods typically employed, a high carbon to mercury mass ratio of 3,000:1 to 50,000:1 is used to achieve a high level of mercury removal [16,18]. Activated carbons can be expensive, with a price of around $500 - 3,000/ton [16,18]. Alternatives to activated carbon injection for point source removal of mercury have been developed both in-house at the National Energy Technology Laboratory and through contracted research funded by the United States Department of Energy [24-35].

The U.S. EPA has announced pending regulation of mercury emissions from U.S. power plants [36,37]. However, these regulations may not reduce the number of fish consumption advisories in the United States. U.S. coal-burning power plants are estimated to have stack emissions of 48 tons of mercury per year [32]. This is approximately 1% of the annual emissions of mercury around the globe from both anthropogenic and natural sources [32]. The growing unregulated emissions of mercury from Asian economies, as well as the global transport of elemental mercury emissions, suggest that other actions may be needed to slow or halt the accumulation of mercury in the food chain.

Passive removal of mercury from air may represent a better solution to the problem [38]. It is proposed that self-cleaning glass, a new and inexpensive product [39-41], could be an important component in the passive collection of mercury from the environment [38].

Self-cleaning glass is coated with titanium dioxide, a well-known photo-oxidation catalyst [39-41]. It can capture mercury from the air as mercuric oxide. The use of self-cleaning glass is envisioned in automobiles and buildings [38]. Mercuric oxide is slightly soluble in water. It can wash down the window with the rain. A thin, unobtrusive, and porous sorbent cartridge, such as activated carbon, can be placed at the bottom of the window in order to capture the mercury [38]. The capacity of the sorbent cartridge is such that it will last the lifetime of the cars and buildings. Proper disposal of the cartridge will prevent mercury from entering the food chain. Automobiles and buildings using these modified windows could constitute millions of passive mobile and stationary collectors of mercury from the air [38]. The concept is similar to that described by Hoke [42] for the use of metal catalyst stripes on automobile radiators for the destruction of air pollutants. Wang [43] described an attempt to alleviate air pollution in Asia by use of titania-coated building materials.Additionally, there are several common band-gap semiconductor oxides, including titanium dioxide, zinc oxide, tin oxide, and iron oxide, which can behave as photocatalysts for the oxidation of mercury [44]. These minerals are common constituents of the earth's crust and are present in the fine particulate matter present in air. These particles are released into the air by volcanoes, forest fires, dust storms, incineration of wastes, and combustion of fossil fuels. It is suggested that the interactions between mercury, long-wave ultraviolet radiation, and band-gap semiconductor oxides play an important role in the global cycling of mercury in the environment.

Experimental

The assembly used for studying the heterogeneous photocatalytic oxidation of mercury is a modified version of an apparatus described earlier [29]. It consists of an elemental mercury permeation tube within an air blending system, and various quartz or pyrex photoreactors with an ultraviolet lamp. Quartz or pyrex are used for the photoreactors because they are transparent to 365-nm light. An 8-in.-long, 6-W ultraviolet lamp from Spectroline (Spectronics BLE-6365S) is used as the source of the 365-nm light. The quartz tubes, pyrex reactors, and titania-coated glass plates are initially cleaned by rinsing first with trace-metals-grade 37% hydrochloric acid, then with distilled water, and last with reagent grade acetone. The permeation tube, located in a heated bath, is held at 212° F in a nitrogen stream at all times and releases 151 ng of elemental Hg/min.

A quartz photoreactor was employed for examination of the removal of mercury from oxygen-nitrogen-carbon dioxide-water vapor mixtures by a high surface area titanium dioxide powder. The fresh titanium dioxide powder contains 0.2 ppm of mercury, and has a BET surface area of 200 m^2/gram. The photoreactor is a 1/4-inch-outer diameter tube described in an earlier paper. A 6 Watt ultraviolet lamp was used as the source of 365-nm radiation in all of the experiments. The intensity of the incident long-wave ultraviolet light upon the powder was 1.0 mW/cm^2. The gas compositions examined were oxygen-nitrogen-carbon dioxide mixtures similar to air. These compositions are:

A: 14% O_2, 270 ppb Hg, 240 ppm CO_2, 86% N_2
B: 21% O_2, 270 ppb Hg, 360 ppm CO_2, 79% N_2
C: 21% O_2, 270 ppb Hg, 360 ppm CO_2, 0-2% H_2O, 77-79% N_2

The gas flow-rate used was 60 ml/min. All experiments were conducted at ambient temperature and pressure.

Samples of the self-cleaning glass were obtained from a PPG-approved supplier. A small pyrex and large pyrex photoreactor were constructed for the glass samples. The small reactor was a 4-cm inner diameter by 25-cm pyrex vacuum trap from Southeastern Laboratory Apparatus. The trap was positioned horizontally over the ultraviolet lamp parallel to its major axis. Smaller irregular-shaped, cut plates were inserted into the reactor with the titania-coated surface face down. Gas was introduced through the center tube and vented from the trap inlet. To reduce bypassing, gas flow in later experiments was directed across the titania-coated glass by use of low density polyethylene bags wadded to produce a baffle and wedged behind the glass sample. Measured light intensities were between 1.2 and 1.8 mW/cm^2.

The large photoreactor was a 4000-ml pyrex kettle. Rectangular-shaped samples (15-cm by 10-cm) of the self-cleaning glass were inserted into the large reactor. The gas stream was introduced by a 0.3-cm outer diameter teflon tube located near the center of the glass samples. Light intensity at the plate surface was approximately 0.4 mW/cm^2.

Cold vapor atomic absorption spectrophotometry (CVAAS) was used to determine the mass of mercury contained on both the used titania powder (yellow in color) and titania-coated glass plates. Acidic solutions were employed to dissolve the mercury; the resulting solutions were analyzed by CVAAS. X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy with energy-dispersive X-ray methods (SEM-EDX) were utilized to confirm the formation of mercuric oxide on the titania surfaces.

Results

A high surface area titania powder was examined in the 1/4-inch photoreactor. The powder was exposed to Gas A for 350 minutes. A large percentage (44.2%) of the mercury was captured as yellow mercuric oxide (Table 4). Little mercury was captured in the absence of long-wave ultraviolet light. These results encouraged further tests with the self-cleaning glass plates.Table 5 shows the mercury levels present in the titania-coated glass blanks. The freshly cleaned glass plates have a very low concentration of mercury (below 0.0001 μg/cm^2). Capture of mercury is not observed upon exposure of the titania-coated glass to Gas A in the absence of long-wave ultraviolet radiation.

The mercury removal by titania-coated glass exposed to Gas A and irradiated by 365-nm light is shown in Table 6. A variable level of mercury was captured by the glass. XPS analysis determined that mercury is present on the surface of the used plates as mercuric oxide. The removal varies with the exposure time and superficial glass surface area. The removals appear to be surface area

limited. The radiation intensity is comparable to mid-day summer incident sunlight in Pittsburgh.

Mercury capture by the glass plates exposed to Gases B and C and irradiated by 365-nm light is presented in Table 7. The presence of water vapor in Gas C appears to significantly enhance the capture of mercury.

There is scatter in the mercury removals obtained by irradiation of Gas C using the 25 cm^2 coated glass plate, as shown by the 33% standard deviation. Several factors impact the uncertainties in the mercury removals. The intensity of light diminishes with the square of the distance from the source. The uncertainty in the distance between the lamp and the photoreactor was ± 1/16 in., introducing an uncertainty in the intensity of 15%. Additionally, an uncertainty in the mercury capture is introduced by the CVAAS analysis. The uncertainty associated with the recovery and CVAAS measurement of mercury is at least ± 10%. The mercury output from the permeation tube has an uncertainty level of at least ± 6%. Therefore, the scatter in the mercury removals is not surprising. Nevertheless, analyses with XPS and SEM-EDX showed that mercury in the oxygen-nitrogen mixtures is oxidized by the titania powder and coated glass, forming mercuric oxide.

Discussion

The screening results shown in Tables 6 and 7 suggest that titania-coated glass plates can sequester mercury from the air. It is noted that the concentration of elemental mercury (270 ppb) used in the experiments is five orders of magnitude greater than the concentration of elemental mercury typically found in ambient air (1 ppt). The extraordinarily small concentration of elemental mercury in air will result in fewer collisions between mercury atoms and the titania surface. This may result in less efficient capture of mercury by titania-coated glass in ambient air.

The addition of water vapor to the oxygen-nitrogen mixtures resulted in a greater level of mercury capture. This result was expected, as both gas phase oxygen and water vapor can serve as oxidants with a titania photocatalyst [44].

In addition, there are other oxidizable compounds present in air, such as methane, hydrogen, carbon monoxide, and sulfur dioxide, shown in Table 2 [45]. It is expected that a titania surface will catalyze the oxidation of these species, possibly in competition with the oxidation of elemental mercury. This may reduce the capture of elemental mercury from air by titania-coated glass plates.

Heterogeneous photocatalytic oxidation can affect the fate of mercury in the atmosphere. Mercuric oxide, associated with fine particulates, has been detected recently in the tropopause [3,4]. Ambient concentrations of elemental mercury in the polar regions has been found to vary with seasonal changes in sunlight [5].

Table 3 lists several common band-gap semiconductors. The bang-gap energies and corresponding maximum excitation wavelengths are tabulated [46]. The maximum excitation wavelengths are typically in the ultraviolet or visible light regions. Photons containing the band-gap energy can induce the formation of reactive radicals such as hydroxyl, as well as other reactive oxygen species, on the semiconductor surface [44]. Kaluza found that elemental mercury can be photooxidized by titania, zinc oxide, tin oxide, and cerium oxide [44]. Kaluza also speculated that hydroxyl radicals (OH) and a chemisorbed charged oxygen species (O_2^-) are responsible for the photooxidation of mercury on titania [44]. Alpha alumina, and silica were found to be inactive photocatalysts for the oxidation of elemental mercury [44].

Various dopants have been previously examined to improve the efficiency of titania photocatalysts for the oxidation of hydrocarbon pollutants. Other band-gap semiconductor oxides have been studied for the oxidation of pollutants. These strategies could be employed in order to improve the capture of elemental mercury by coated glass, as well as to enhance the self-cleaning properties of the windows.

It is currently thought that elemental mercury is removed from the atmosphere by gas phase oxidation by ozone and hydroxyl radicals, viz [8]:

$$Hg_{(gas)} + OH_{(gas)} \rightarrow HgO_{(gas)} + H_{(gas)} \quad (2)$$

Reaction (1) is the gas phase oxidation of elemental mercury by ozone to form mercuric oxide. Reaction (2) is the gas phase oxidation of elemental mercury by hydroxyl radical to form mercuric oxide and a hydrogen radical. The gas-phase concentrations of elemental mercury, ozone, and hydroxyl, as well as the rate constants for reactions (1) and (2) are consistent with the long half life of elemental mercury in the atmosphere [8].

In the polar regions, halogen and halogen oxide radicals originating from sea spray are hypothesized to oxidize mercury, viz [10]:

$$Br/Cl_{(gas)} + O_{3(gas)} \rightarrow ClO/BrO_{(gas)} + O_{2(gas)} \quad (3)$$
$$BrO/ClO_{(gas)} + Hg_{(gas)} \rightarrow HgO_{(gas)} + Br/Cl_{(gas)} \quad (4)$$
$$Hg_{(gas)} + 2\ Br/Cl_{(gas)} \rightarrow HgBr_2/HgCl_{2(gas)} \quad (5)$$

Reaction (3) is the photochemical depletion of ozone by halogens. Reaction (4) is the gas phase oxidation of elemental mercury by halogen oxides to form mercuric oxide and halogen radicals. Reaction (5) is the oxidation of elemental mercury by halogen radicals to form gas phase mercuric chloride and mercuric bromide. This mechanism has been proposed by Lindberg in order to account for the depletion of ambient elemental mercury observed during springtime polar sunrise [10].

The heterogeneous photooxidation of elemental mercury by band-gap semiconductors is another potential route for the deposition of mercury. The overall reactions can be crudely represented by equations (6) and (7):

$$Hg_{(gas)} + \text{band-gap particle} + \text{light} + O_{2(gas)} \rightarrow HgO_{(ad)} + \text{radicals}_{(surf)} \quad (6)$$

$$Hg_{(gas)} + \text{band-gap particle} + \text{light} + H_2O_{(gas)} \rightarrow HgO_{(ad)} + \text{radicals}_{(surf)} \quad (7)$$

The surface radicals or charged oxygen entities can recombine to form oxygen or water, or react with other

oxidizable adsorbed species. Band-gap semiconductors which potentially could participate in reactions (6) and (7) include titanium oxide, zinc oxide, tin oxide, iron oxide, cerium oxide, and carbon. Xie found titanium and zinc present in Arctic aerosols [9]. The ubiquitous nature of these common fine band-gap semiconductor particulates suggests that they may play a role in the oxidation of elemental mercury in the atmosphere. Schroeder had earlier found mercuric oxide associated with fine particulates in the upper atmosphere of the Arctic [5].

The possibility that carbon fine particles can act as heterogeneous photocatalysts for the oxidation of elemental mercury requires further examination. The band-gap energy of carbon (Table 3) suggests that short wave ultraviolet radiation is required for it to behave as a photocatalyst for the oxidation of mercury. This could occur in the upper atmosphere, where short wave ultraviolet light is more prevalent than in the lower atmosphere.

Conclusions

Photo-oxidation of mercury with self-cleaning glass is a method for sequestration from ambient air. A preliminary estimate suggests that a substantial quantity of mercury could be removed from the atmosphere by wide-scale utilization of the self-cleaning glass-sorbent cartridge apparatus. Passive removal of mercury from air has several advantages over costly point source removal techniques and is a unique approach to the problem of mercury in the food chain. Capture of elemental mercury from oxygen-nitrogen mixtures has been demonstrated. The intensity of the incident long-wave ultraviolet radiation is comparable to sunlight. Passive removal of mercury should be reliable as no moving parts or external power supplies are necessary. The presence of moisture resulted in higher levels of mercury capture, possibly due to the formation of hydroxyl radicals on the glass surface. Future research should focus on mercury capture from more dilute mercury mixtures (at part per trillion by volume levels) representative of air. The effect of other oxidizable species present in air (such as methane, hydrogen, carbon monoxide, and sulfur dioxide) upon the removal of mercury needs to be determined. Other band-gap semiconductor oxide coatings should be studied for the capture of elemental mercury, as well as to enhance the self-cleaning properties of the windows.

Sunlight is a major factor in the transport and transformations of mercury in the environment. The interactions of mercury with band-gap semiconductor oxides may be a significant factor in the global mercury cycle. The ubiquitous nature of long-wave ultraviolet radiation and band-gap semiconductor oxide fine particles suggests that they drive the atmospheric transformations of mercury between the elemental, oxidized, and particulate-bound forms. Photo-oxidation by band-gap semiconductor oxide fine particles could be a factor in the seasonal fluctuations of elemental mercury in the atmosphere. Photocatalytic oxidation of elemental mercury by carbon particulates, if confirmed, would have major implications for the global cycle of mercury.

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Disclaimer

Reference to any specific commercial product or service is to facilitate understanding and does not imply endorsement by the United States Department of Energy.

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Table 1. Typical Untreated Flue Gas Composition From a Pulverized Coal Combustor Burning a Low-Sulfur Bituminous Coal [16, 29]

Species	Concentration (by volume)
H_2O	5-7%
O_2	3-4%
CO_2	15-16%
total Hg	1 ppb
CO	20 ppm
hydrocarbons	10 ppm
HCl	100 ppm
SO_2	800 ppm
SO_3	10 ppm
NO_x	500 ppm
N_2	balance

Table 2. Typical Composition of Air (Dry-Basis) Near Sea Level [8, 45]

Component	Concentration (by volume)
N_2	78.1 %
O_2	20.9 %
Noble Gases	0.9 %
Total Hg	1 ppt
CO_2	360 ppm
CH_4	2 ppm
H_2	0.5 ppm
CO	trace
SO_2	trace
NO_2	trace
others	balance

Table 3. Band-Gap Semiconductors Present in Air [46]

Semiconductor	Band-Gap E_{gap} (eV)	Maximum Excitation Wavelength $\lambda_{max} = hc/E_{gap}$ (nm)	
TiO_2	3.0	414	(long wave ultraviolet)
ZnO	3.2	388	(long wave ultraviolet)
Fe_2O_3	2.0	620	(visible light)
SnO_2	3.6	345	(long wave ultraviolet)
CeO_2	3.2	388	(long wave ultraviolet)
Carbon	5.2	239	(short wave ultraviolet)

Table 4. Mercury Capture By Titania Powder

Gas	Exposure (min)	Mercury Capture (%)
A	350	44.2
A (No UV)	350	1.2

Table 5. Mercury Levels in Titania-Coated Glass Blanks

Glass Area cm^2	Exposure (min)	Loading µg Hg/cm^2
155	0	less than 0.0001
16	0	less than 0.0001
155 (Gas A)	300 (no UV)	less than 0.0001

Table 6. Mercury Capture By Titania-Coated Glass Plates: Small Reactor, Gas A

Glass Area cm^2	Exposure (min)	Loading µg Hg/cm^2	% Mercury Capture
16	350	0.2	5.9
155	360	0.03	8.9
33	745	0.37	10.1
16	990	0.16	1.8
139	990	0.48	42.4
5	1050	0.23	0.7
33	1369	0.22	3.2
4	2490	0.47	0.5

Table 7. Mercury Capture By Titania-Coated Glass Plates: Gases B&C

Glass Area cm^2		Exposure (min)	Loading µg Hg/cm^2	% Mercury Capture
25	Gas B	990	0.03	0.5
25	Gas C	995	0.51	8.5
25	Gas C	3900	5.0	21.2
25	Gas C	4065	7.0	28.7
25	Gas C	3900	3.4	14.4