Environ. Sci. Technol. **2006**, *40,* 6444−6448

Role of Moisture in Adsorption, Photocatalytic Oxidation, and Reemission of Elemental Mercury on a SiO_2-TiO_2 Nanocomposite

YING LI AND CHANG-YU WU*
Department of Environmental Engineering Sciences, University of Florida, P.O. Box 116450, Gainesville, Florida 32611-6450

A novel silica−titania (SiO_2-TiO_2) nanocomposite has been developed to effectively capture elemental mercury (Hg^0) under UV irradiation. Moisture has been reported to have an important impact on this nanocomposite's performance. In this work, the role of moisture on Hg^0 removal and reemission as well as the corresponding mechanisms was investigated. Hg^0 removal experiments were carried out in a fixed-bed reactor at 65 °C using air as the carrier gas. Without UV irradiation, Hg^0 adsorption was found to be insignificant, but it could be enhanced by the photocatalytic oxidation product, mercuric oxide (HgO), possibly due to the high affinity between HgO and Hg^0. Under dry conditions 95% of Hg^0 can be removed; however, increased humidity levels remarkably suppress both Hg^0 adsorption and photocatalytic oxidation. Introducing water vapor can also result in significant reemission of captured Hg^0 from the nanocomposite, which may be ascribed to the repellant effect of water vapor adsorbed on the superhydrophilic TiO_2 surface. Exposure to UV light was found either to prohibit Hg^0 reemission when photocatalytic oxidation of reemitted Hg^0 prevailed or to promote Hg^0 reemission when photocatalytic reduction of HgO to Hg^0 dominated later on. The results indicate that minimization of Hg^0 reemission can be achieved by appropriate application of UV irradiation.

Introduction

Mercury (Hg) was identified as one of the hazardous air pollutants (HAPs) in the 1990 Clean Air Act Amendments (CAAA). Hg tends to bioaccumulate in the food chain and is toxic to humans (*1*). According to the *Mercury Study Report to Congress* prepared by the U.S. Environmental Protection Agency (USEPA) (*2*), the major anthropogenic Hg emission sources are coal-fired boilers, municipal waste combustors, and medical waste incinerators. Hg emissions from manufacturing sources are generally lower compared to combustion sources with the exception of chlor-alkali plants using the mercury cell process and portland cement manufacturing plants (*2*). Ever since the 1990 Clean Air Act, the U.S. EPA has issued a series of rules to regulate Hg emissions from solid waste combustors/incinerators (*3*, *4*), mercury cell chlor-alkali plants (*5*), and coal-fired power plants (*6*). Consequently, numerous technologies have been developed to offer high levels of Hg control from various Hg emission sources.

A novel low-cost methodology using titanium dioxide (TiO_2) nanoparticles as a photocatalyst has been recently developed to effectively remove elemental mercury (Hg^0) from exhaust air (*7*−*9*). Under ultraviolet (UV) irradiation, hydroxyl (OH) radicals are generated on the surface of TiO_2 and oxidize Hg^0 to form mercuric oxide (HgO), which is then retained on the particle surface. Wu et al. (*7*) and Lee et al. (*8*) reported a high level of Hg^0 capture in simulated combustor exhaust using TiO_2 particles generated in situ, while Pitoniak et al. (*9*) used a highly porous silica (SiO_2) gel doped with TiO_2 nanoparticles and achieved synergistic adsorption and photocatalytic oxidation of Hg^0 in a fixed-bed reactor. The high surface area and open structure of the SiO_2-TiO_2 nanocomposite allow effective irradiation by UV light and thus minimize the mass-transfer resistance for Hg^0 (*7*, *9*). Potential applications of the SiO_2-TiO_2 nanocomposite for Hg removal lie in two main areas. First, a powdered form of the nanocomposite can be injected into combustion exhaust upstream of a particle control device. Second, the nanocomposite can be used in packed-bed columns to treat Hg emissions from various sources such as chlor-alkali plants and portland cement plants.

Among the factors that affect the efficiency of Hg^0 capture by the TiO_2 photocatalyst, moisture content in the Hg^0-laden gas was reported to be one of the most important (*9*, *10*). Using in-situ generated TiO_2 nanoparticles in a flow reactor, Rodríguez et al. (*10*) developed a mechanistic model and reported that Hg^0 capture was promoted by low water vapor concentrations (700−1800 ppm_v) but remained constant at higher water vapor concentrations. They also speculated that very high water vapor concentrations can inhibit Hg^0 oxidation by occupying available adsorption sites. Using a SiO_2-TiO_2 nanocomposite in a fixed-bed flow reactor, Pitoniak et al. (*9*) reported that when the relative humidity increased from 15% to 90% at room temperature, the rate of Hg^0 adsorption decreased but that the rate of photocatalytic oxidation remained constant.

While there is limited understanding of the effect of water vapor on Hg^0 capture on TiO_2 surfaces, many research studies have investigated the effect of water vapor on photodegradation of organic pollutants in air streams using TiO_2 nanoparticles or thin films. Obee and Hay (*11*) reported that moisture in the range 0−25 000 ppm_v inhibited photooxidation of ethylene by a TiO_2-coated glass plate. Shang et al. (*12*) found that water vapor at concentrations of 3.7−22.4 g m^{-3} inhibited photocatalytic oxidation of heptane in a quartz reactor coated with TiO_2 particles. It was also reported that water vapor strongly inhibits the oxidation of trichloroethylene (TCE) and acetone (*13*) but enhances the oxidation of toluene (*13*, *14*). The results obtained using batch reactors coated with TiO_2 thin films were consistent with those using flow reactors packed with TiO_2 particles. These findings indicate that water vapor can either promote or inhibit photocatalyitc oxidation of different organic pollutants. This uncertainty about the effect of water vapor necessitates further investigation of the effect of moisture on Hg^0 oxidation by TiO_2-based photocatalysts.

The goal of this study was to probe the role of moisture on Hg^0 capture (adsorption and/or photocatalytic oxidation) using a SiO_2-TiO_2 nanocomposite. This study did not aim to explore the maximum Hg removal efficiency under certain emission conditions. Thus, the experimental conditions used in this study (65 °C gas temperature and up to 23 000 ppm_v H_2O) were designed to explore the range of emission conditions encountered in various combustion and manufacturing processes and not to be representative of any

---

* Corresponding author phone: 352-392-0845; fax 352-392-3076; e-mail: cywu@ufl.edu.

10.1021/es061228a CCC: $33.50

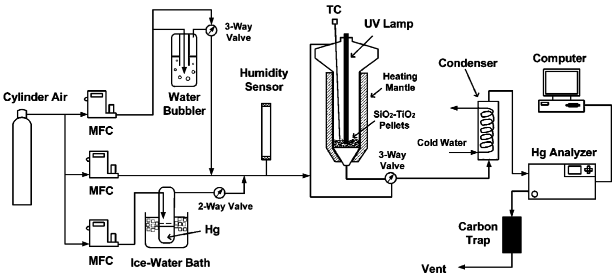

FIGURE 1. Schematic diagram of the experimental system.

specific process. In this study, possible reemission of captured Hg species was also examined, to provide an overall evaluation of the performance of the SiO_2-TiO_2 nanocomposite. The corresponding mechanisms of Hg^0 removal and re-emission were investigated as well.

Experimental Section

Synthesis of SiO_2-TiO_2 Nanocomposite. The SiO_2-TiO_2 nanocomposite was made by a sol−gel method using deionized water, ethanol, and tetraethyl orthosilicate (TEOS). Nitric acid (HNO_3) and hydrogen fluoride (HF) were used as catalysts to increase the hydrolysis and condensation rates. A detailed synthetic procedure has been reported by Pitoniak et al. (*9*). The nanocomposite was prepared in the form of cylindrical pellets approximately 5 mm in length and 3 mm in diameter. The weight fraction of TiO_2 in the prepared SiO_2-TiO_2 nanocomposite was approximately 13%.

Experimental Setup. A schematic diagram of the experimental system is shown in Figure 1. The incoming air flow was divided into three streams, the flow rates of which were controlled by mass flow controllers (FMA 5400/5500, Omega). The total flow rate remained constant at 2 L/min. One of the air streams was allowed to pass through a water bubbler (to provide a humid flow) or to bypass it for dry conditions. The second stream served as dilution to adjust the humidity level. The third stream passed through the surface of a liquid Hg^0 reservoir and introduced Hg^0-vapor-laden air into the system. The Hg^0 reservoir was placed in an ice−water bath to maintain a constant Hg^0 vapor pressure. After the three streams converged, a humidity sensor (HX94C, Omega) was used to measure the relative humidity, from which the partial pressure (volume fraction) of water can be calculated.

Downstream was the fixed-bed photocatalytic reactor, the lower part of which was a cylindrical tube of fused quartz 4.5 cm in diameter and 20 cm in length. The gas stream passed through the reactor from top to bottom. The reactor was mounted with a fused quartz center 2 cm in diameter, which was used to house a UV lamp. The UV light delivered 4 mW/cm^2 intensity measured by a UVX radiometer (with a UVX-36 sensor probe) at a peak wavelength of 365 nm. Aluminum foil was wrapped around the cylindrical tube to reflect UV energy. A heating mantle (regulated by a temperature controller) was used to heat the reactor to each selected temperature, which was monitored by a thermocouple (type K, Omega). At the bottom of the reactor a glass frit was used to hold the SiO_2-TiO_2 pellets within the bed. In this study, 2.5 g of fresh pellets was used in each test, which gave an average bed thickness of 4 mm (approximately one layer of pellets). Before each test, the pellets were heated at 130 °C for 3 h to remove any moisture that may have adsorbed from the storage environment.

A RA-915+ Hg analyzer (OhioLumex) was used to measure Hg^0 concentration at the outlet of the reactor. The Hg analyzer is based on Zeeman atomic absorption spectrometry, which is selective only for Hg^0 and capable of providing a real-time response every 1 s. The calibration of the Hg analyzer was conducted by the manufacturer using a Dynacal permeation device, which is certified traceable to NIST (National Institute of Standards and Technology) standards. In this study, the high-concentration mode of the analyzer was used (with a detection limit of 0.5 $\mu g\ m^{-3}$ and an upper measurable concentration of 200 $\mu g\ m^{-3}$). A condenser was installed upstream of the Hg analyzer to remove excess moisture in the gas stream to minimize possible interference from water vapor. Although a Hg speciation converting unit could be used to analyze both Hg(II) and Hg^0 in the gas phase, it was not installed in this study. This is because HgO is the only product for the reaction between Hg^0 and hydroxyl radicals (*15*, *16*) and its extremely low saturation vapor pressure, 9.2×10^{-12} Pa at 25 °C (*17*), causes HgO to deposit on the catalyst in the reactor. Baseline Hg^0 concentration was obtained when the Hg^0-laden air bypassed the reactor. The Hg^0 removal efficiency was obtained by comparing the outlet Hg^0 concentration with the baseline level. Finally, the air stream was passed through a carbon trap before it was exhausted into the fume hood.

Results and Discussion

Role of Moisture in Hg^0 Capture. To investigate the effect of moisture on Hg^0 capture by the SiO_2-TiO_2 nanocomposite, experiments were conducted at different water vapor concentrations (0, 13 000, and 23 000 ppm$_v$). Blank runs without the nanocomposite were performed at concentrations of around 65 $\mu g\ m^{-3}$ Hg^0 and 0 and 23 000 ppm$_v$ water vapor. Less than 0.5% reduction in Hg^0 concentration was observed when the Hg^0-laden air passed through the reactor with or without UV light. Tests were also conducted to examine any possible interference of water vapor on measurements by the Hg analyzer. While exactly the same experimental parameters were maintained, variations in the Hg readings were less than 1% when switching from a dry to a humid (23 000 ppm$_v$ H_2O) condition, indicating negligible interference from water vapor in this range.

In each experiment, the baseline Hg^0 concentration (Hg^0_{BL}, ~65 $\mu g\ m^{-3}$) was measured first. Then the Hg^0-laden air was passed through the reactor for 10 min and concentrations defining the initial adsorption (IA) of Hg^0 were recorded. Next, the UV light was turned on for 10 min—allowing photocatalytic oxidation of Hg^0 to take place—and then turned off for 5 min. Another two such UV on/off cycles were repeated, and concentrations defining the final removal (FR) efficiency were recorded. After that, Hg^0_{BL} was checked again, and the Hg^0-laden air was passed through the reactor without UV for 15 min. Finally concentrations to compute the adsorption at the end of the test (EA) were recorded.

The temperature at the pellet surface was maintained near 65 °C throughout the experiment. Measured 5 mm above the pellets, the temperature of the gas passing through the pellets was approximately 1.5 °C lower than that of the pellets. To maintain a relatively constant temperature, the heating mantle around the reactor was turned off when the UV lamp was switched on in each cycle and back on when UV was switched off. The fluctuations in temperature of both pellets and gas were measured to be ±2 °C. A preliminary test showed that the change in the final removal efficiency was less than 5% when the average temperature of the pellets increased from 65 to 70 °C. This indicated that the fluctuations within this range of temperature had negligible effects on the reaction rate.

Figure 2 shows the dimensionless Hg^0 concentration [Hg^0/Hg^0_{BL}] at the outlet of the reactor in dry and humid conditions. Under dry conditions (Figure 2A), Hg^0 removal efficiency increased with successive cycles and FR reached 95% during the fourth irradiation. Adsorption was initially insignificant (IA = 5%), but it was enhanced at the end of the test (EA = 22%). In contrast, when the water vapor concentration was increased to 13 000 ppm$_v$ (Figure 2B), Hg^0 removal increased

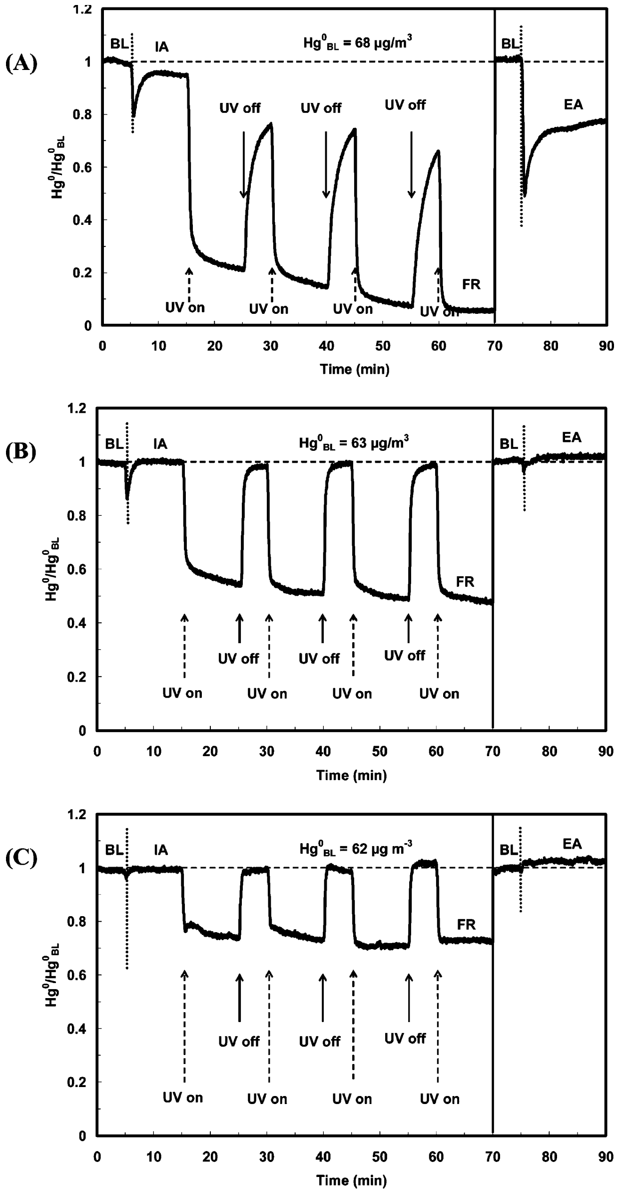

FIGURE 2. Dimensionless Hg^0 concentration at the reactor outlet (A, $[H_2O] = 0$ ppm$_v$; B, $[H_2O] = 13\ 000$ ppm$_v$; C, $[H_2O] = 23\ 000$ ppm$_v$).

only slightly with successive cycles and FR ended at only 51%. When the water vapor concentration was further increased to 23 000 ppm$_v$ (Figure 2C), FR decreased to 28%.

In addition, Hg^0 adsorption was found to be insignificant throughout the test under these two humid conditions. A separate test was conducted extending the adsorption time to 2 h (without UV), and no adsorption was observed. This verified that the recorded values of IA and EA were measured at adsorption equilibrium. Experiments under the three humidity conditions were repeated, and similar results were recorded. The results indicated that increased humidity can significantly suppress both Hg^0 adsorption and photocatalytic oxidation on the nanocomposite.

Role of Moisture in Hg^0 Reemission. Potential reemission of Hg species from the SiO_2-TiO_2 nanocomposite after their capture is an important factor in evaluating the overall performance of the nanocomposite. The experiment to examine Hg reemission began by exposing 2.5 g of fresh pellets for 3 h to UV light in a stream containing approximately 300 μg/m³ Hg^0 vapor in dry air at room temperature. During the 3-h pretreatment, Hg^0 capture efficiency by the nanocomposite reached about 90% after 30 min and remained relatively steady between 90 and 95% for the rest of the time (as shown in the insert in Figure 3). The Hg species retained on the nanocomposite are predicted to be a mixture of HgO (due to photocatalytic oxidation) and Hg^0 (due to adsorption enhanced by HgO) (*18*).

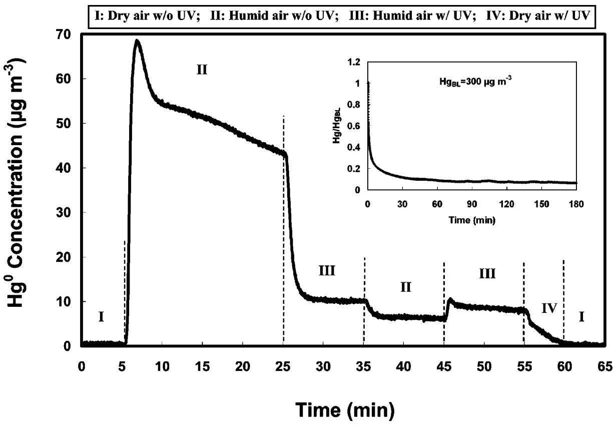

FIGURE 3. Hg^0 reemission from SiO_2-TiO_2 nanocomposite after 3-h pretreatment.

After the pretreatment, Hg^0 release from the nanocomposite at room temperature was examined by feeding Hg^0-free air into the reactor (see Figure 3). During the first 5 min, dry air (condition I) was allowed to pass through the pretreated pellets and only traces of reemitted Hg^0 were found. However, immediately after the air stream was switched from dry to humid ($[H_2O] = 23\ 000$ ppm$_v$, condition II), a significant release of Hg^0 was observed, peaking briefly at 68 g/m³, about 23% of the Hg^0 feeding level during pretreatment. Even though the Hg^0 reemission level decreased over time, it remained relatively high (43 μg/m³) after 20 min. Hg^0 reemitted during this 20-min period was calculated to be approximately 2.1% of the total Hg species (Hg^0 and HgO) retained on the pellets during the 3-h pretreatment.

At 25 min, UV light was turned on while the air stream remained humid (condition III), and the Hg^0 concentration quickly dropped to approximately 10 μg/m³. This suggests that a large portion of the Hg^0 reemitted was photooxidized during irradiation. At 35 min, the UV light was turned off (return to condition II), and the rate of Hg^0 reemission did not recover to the previous high level but further decreased to approximately 6.5 μg/m³. Turning the UV on again (return to condition III) at 45 min caused the Hg^0 concentration to return to an extrapolation of the line observed during the first period at condition III. When the condition was switched at 55 min to dry air with UV on (condition IV), the Hg^0 concentration decayed to approximately zero in 5 min. The results of the reemission test were repeatable using another batch of pellets undergoing the same pretreatment procedure.

One may draw three conclusions about Hg^0 reemission under the conditions tested: (1) Hg^0 reemission does not occur in dry air, with or without UV light. (2) Introducing water vapor causes significant Hg^0 reemission, which slowly decreases over time. (3) Exposure to UV light in humid air can either inhibit or promote Hg^0 reemission.

Mechanisms of Hg^0 Capture and Reemission. To explain these intriguing findings, a comprehensive model is developed in this work elucidating the fate of Hg species on the surface of this SiO_2-TiO_2 nanocomposite. In this model, as illustrated in Figure 4, Hg^0 capture is accomplished by photocatalytic oxidation and adsorption, while Hg^0 reemission results from desorption and photocatalytic reduction.

Photocatalytic oxidation of Hg^0 occurs during UV irradiation of the SiO_2-TiO_2 nanocomposite, as shown in Figure 4a. Hg^0 is oxidized by OH radicals generated on the TiO_2

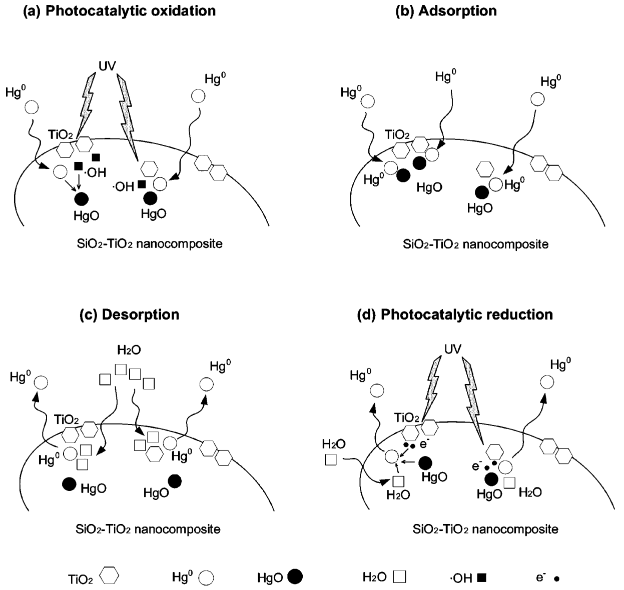

FIGURE 4. Mechanisms of Hg capture and reemission on the surface of SiO_2-TiO_2 nanocomposite.

surface, and HgO has been reported to be the final oxidation product in literature (*8–10, 15, 16, 18*). Pal and Ariya (*15*) experimentally identified HgO as the only product for gas-phase reaction of Hg^0 with OH radicals, while HgOH was suggested to be an intermediate reaction product (*10*, *15*, *16*) that has a very short lifetime (*19*). The fast removal of Hg^0 in this study (see Figure 2) was consistent with rates reported by Pitoniak et al. (*9*, *18*) using similar experimental systems. It was faster than OH–Hg reactions reported under simulated atmospheric conditions (*15*, *16*, *20*), most likely due to the much higher concentration of OH radicals produced on the high-surface-area, open-structured SiO_2-TiO_2 nanocomposite. The overall mechanism of photocatalytic oxidation can be described by the following reactions:

$$TiO_2 + h\nu \rightarrow e^- + h^+ \tag{1}$$

$$H_2O \leftrightarrow H^+ + OH^- \tag{2}$$

$$h^+ + OH^- \rightarrow {}^{\bullet}OH \tag{3}$$

$$h^+ + H_2O \rightarrow {}^{\bullet}OH + H^+ \tag{4}$$

$$OH^{\bullet} + Hg^0 \xrightarrow{\text{overall}} HgO \tag{5}$$

It should be noted that the specifications of the cylinder air indicated a water vapor concentration of less than 24 ppm_v. This low concentration of water vapor could not be detected by the humidity sensor, and thus, the air was considered “dry.” However, this water vapor concentration is 3 orders of magnitude higher than that of Hg^0 used in this study. Further, the SiO_2-TiO_2 pellets have a great capacity to adsorb water vapor. Tests demonstrated that 2.5 g of SiO_2-TiO_2 pellets can adsorb an average of 0.16 g of water vapor in 30 min when exposed to an air flow containing 23 000 ppm_v water vapor. Therefore, even though the pellets were pretreated at 130 °C for 3 h before each experiment to remove any interior moisture, they adsorbed enough moisture (compared to the trace amount of Hg^0) from the cylinder air to support the generation of OH radicals and subsequent photocatalytic oxidation.

Physisorption of Hg^0 is minor if the SiO_2-TiO_2 nanocomposite is not exposed to UV light, but it can be enhanced by HgO that is deposited on the composite's surface after photocatalytic oxidation takes place (Figure 4b). This is likely due to the high affinity between Hg^0 and HgO, which was characterized by a decrease in the contact angle of Hg on the HgO-enriched sorbent surface (*18*). However, this enhanced adsorption ability was not observed in humid conditions due to the inhibitory effect of water vapor.

It is generally believed that water vapor inhibits photocatalytic reactions by blocking the available adsorption sites on the surface of TiO_2 catalysts (*9*, *12*, *13*). The results of this study suggest that desorption of bound Hg^0 by a high concentration of water vapor (Figure 4c) also contributes to the reduced Hg^0 capture rate. The reason is likely related to the photoinduced superhydrophilicity of TiO_2 surfaces (*21*, *22*). During the process of photocatalysis, the electrons tend to reduce the Ti(IV) cations to the Ti(III) state, and the holes oxidize the O^{2-} anions. In the process, oxygen atoms are ejected, creating oxygen vacancies. Water molecules can then occupy these oxygen vacancies and create adsorbed OH groups, which tend to make the surface hydrophilic. Hence, in our experiments, when humid air passed through the reactor, the superhydrophilic surface of TiO_2 may attract excessive amount of water and result in ejection of adsorbed Hg^0 (which is superhydrophobic) from the surface (Figure 4c). This mechanism is similar to the self-cleaning (stain proofing) quality of TiO_2-coated glass (*22*, *23*), from which organic stains are washed away by rainfall (or water) on the superhydrophilic surface.

A sharp decrease in Hg^0 concentration was detected when switching from the initial condition II to III (Figure 3). A very possible reason is that the desorbed Hg^0 was reoxidized upon UV irradiation and recaptured onto the pellets. However, the increase in Hg^0 concentration when switching from the second condition II to III indicated that UV irradiation contributed to the reemission of Hg^0 from the pellets. This can be explained by the photocatalytic reduction of HgO to Hg^0 by the free electrons generated on TiO_2 surface under UV light (Figure 4d). The mechanism is expressed in reaction 6, which has a reduction potential of 0.098 V vs normal hydrogen electrode (NHE) (*24*):

$$HgO + H_2O + 2e^- \rightarrow Hg + 2OH^- \tag{6}$$

To validate the occurrence of reaction 6 in this study, its redox potential was compared with those in other photocatalytic reactions on TiO_2 reported in the literature. Fujishima et al. (*22*) reported reduction of O_2 to H_2O_2 on a TiO_2 photocatalyst. Zhang et al. (*25*) used TiO_2-modified sewage sludge carbon for photocatalytic removal and recovery of Hg^{2+} in the form of Hg^0 from water. The redox potentials of O_2/H_2O_2 and Hg^{2+}/Hg are 0.28 V (*22*) and 0.85 V (*24*), respectively. Thus, it is reasonable to infer that reaction 6, which has a much lower redox potential (0.098 V), can occur in our system. The necessity of H_2O in reaction 6 is also consistent with the finding that no Hg^0 reemission occurred in dry air with UV irradiation.

Separate experiments were conducted in pure O_2 and N_2, respectively, and the results further supported the hypothesis that photocatalytic reduction caused the reemission of Hg^0. Under humid conditions and UV irradiation, a higher Hg^0 reemission level was observed in N_2 than in O_2. Because the redox potential of O_2/O_2^- (−0.28 V) is lower than that of HgO/Hg, O_2 is a stronger electron trap than HgO. The absence of O_2 increased the chance for HgO to trap electrons, and thus more HgO was reduced to Hg in pure N_2.

The intriguing finding that UV irradiation can result in either inhibition or promotion of Hg^0 reemission (as shown in Figure 3) can then be explained by the competition between photocatalytic oxidation of reemitted Hg^0 to form HgO (reaction 5) and photocatalytic reduction of HgO to form Hg^0 (reaction 6), accompanied by the physical desorption of

Hg^0 caused by water vapor at the same time. At the moment when the condition was first changed from II to III, the concentration of desorbed Hg^0 was very high, and thus photocatalytic oxidation prevailed over reduction, which resulted in a sharp decrease in Hg^0 concentration. Over time, the rate of photocatalytic oxidation decreased as the Hg^0 desorption rate decreased. When the condition was switched from II to III for the second time, the rate of photocatalytic oxidation dropped to a lower level than that of photocatalytic reduction, so the level of Hg^0 reemission increased.

The above discussion boils down to a conclusion that Hg^0 capture on the SiO_2-TiO_2 nanocomposite in a humid environment under UV irradiation is controlled by four mechanisms: adsorption; photocatalytic oxidation; desorption; photocatalytic reduction. Water vapor concentration is a significant parameter affecting the Hg^0 capture efficiency. The inhibitory effect of water vapor is due to its competitive occupancy of the available adsorption sites, displacement of adsorbed Hg^0, and participation in the photocatalytic reduction of HgO to Hg^0.

Hg^0 reemission seems to be inevitable since humidity exists in most environmental conditions. However, the mechanisms discussed above imply that appropriate application of UV irradiation can be utilized to mitigate this Hg^0 reemission. The difference between the first and second condition II in Figure 3 shows that UV treatment caused a significant drop of the Hg^0 reemission level. However, further exposure to UV light caused an increase in the Hg^0 reemission due to the dominant photocatalytic reduction later on. Therefore, determining the optimal time of UV treatment and avoiding further exposure to UV sources (including sunlight) are critical to achieving minimal Hg^0 reemission.

Acknowledgments

We are thankful for the support by the STAR program of the U.S. EPA under Grant No. R-82960201. We are also grateful for insightful inputs from Dr. Wolfgang Sigmund at University of Florida and Dr. Joseph Wander at Air Force Research Lab.

Literature Cited

(1) Brown, T. D.; Smith, D. N.; Hargis, R. A.; O'Dowd, W. J. Mercury measurement and its control: What we know, have learned, and need to further investigate. *J. Air Waste Manage. Assoc.* **1999**, *49*, 628−640.

(2) *Mercury Study Report to Congress*; U.S. Environmental Protection Agency: Washington, DC, 1997; EPA-452/R-97-003.

(3) U.S. Environmental Protection Agency. Standards of Performance for New Stationary Sources and Emission Guidelines for Existing Sources: Hospital/Medical/Infectious Waste Incinerators; Final Rule. *Fed. Regist.* **1997**, *62*, 48347−448391.

(4) U.S. Environmental Protection Agency. Standards of Performance for Large Municipal Waste Combustors; Final Rule and Proposed Rule. *Fed. Regist.* **2001**, *66*, 57823−57828.

(5) U.S. Environmental Protection Agency. National Emission Standards for Hazardous Air Pollutants: Mercury Emissions from Mercury Cell Chlor-Alkali Plants; Final Rule. *Fed. Regist.* **2003**, *68*, 70903−70946.

(6) U.S. Environmental Protection Agency. Standards of Performance for New and Existing Stationary Sources: Electric Utility Steam Generating Units: Final Rule. *Fed. Regist.* **2005**, *70*, 28606−28700.

(7) Wu, C. Y.; Lee, T. G.; Tyree, G.; Arar, E.; Biswas, P. Capture of mercury in combustion systems by in-situ generated titania particles with UV irradiation. *Environ. Eng. Sci.* **1998**, *15*, 137−148.

(8) Lee, T. G.; Biswas, P.; Hedrick, E. Comparison of Hg^0 capture efficiencies of three in situ generated sorbents. *AIChE J.* **2001**, *47*, 954−961.

(9) Pitoniak, E.; Wu, C. Y.; Londeree, D.; Mazyck, D.; Bonzongo, J. C.; Powers, K.; Sigmund, W. Nanostructured silica-gel doped with TiO_2 for mercury vapor control. *J. Nanopart. Res.* **2003**, *5*, 281−292.

(10) Rodriguez, S.; Almquist, C.; Lee, T. G.; Furuuchi, M.; Hedrick, E.; Biswas, P. A mechanistic model for mercury capture with in situ-generated titania particles: Role of water vapor. *J. Air Waste Manage. Assoc.* **2004**, *54*, 149−156.

(11) Obee, T. N.; Hay, S. O. Effects of moisture and temperature on the photooxidation of ethylene on Titania. *Environ. Sci. Technol.* **1997**, *31*, 2034−2038.

(12) Shang, J.; Du, Y. G.; Xu, Z. L. Photocatalytic oxidation of heptane in the gas-phase over TiO_2. *Chemosphere* **2002**, *46*, 93−99.

(13) Kim, S. B.; Hong, S. C. Kinetic study for photocatalytic degradation of volatile organic compounds in air using thin film TiO_2 photocatalyst. *Appl. Catal., B: Environ.* **2002**, *35*, 305−315.

(14) Augugliaro, V.; Coluccia, S.; Loddo, V.; Marchese, L.; Martra, G.; Palmisano, L.; Schiavello, M. Photocatalytic oxidation of gaseous toluene on anatase TiO_2 catalyst: mechanistic aspects and FT-IR investigation. *Appl. Catal., B: Environ.* **1999**, *20*, 15−27.

(15) Pal, B.; Ariya, P. A. Gas-phase HO-Initiated reactions of elemental mercury: Kinetics, product studies, and atmospheric implications. *Environ. Sci. Technol.* **2004**, *38*, 5555−5566.

(16) Sommar, J.; Gardfeldt, K.; Stromberg, D.; Feng, X. B. A kinetic study of the gas-phase reaction between the hydroxyl radical and atomic mercury. *Atmos. Environ.* **2001**, *35*, 3049−3054.

(17) Schroeder, W. H.; Munthe, J. Atmospheric mercury-An overview. *Atmos. Environ.* **1998**, *32*, 809−822.

(18) Pitoniak, E.; Wu, C. Y.; Mazyck, D. W.; Powers, K. W.; Sigmund, W. Adsorption enhancement mechanisms of silica-titania nanocomposites for elemental mercury vapor removal. *Environ. Sci. Technol.* **2005**, *39*, 1269−1274.

(19) Goodsite, M. E.; Plane, J. M. C.; Skov, H. A theoretical study of the oxidation of Hg^0 to $HgBr_2$ in the troposphere. *Environ. Sci. Technol.* **2004**, *38*, 1772−1776.

(20) Calvert, J. G.; Lindberg, S. E. Mechanisms of mercury removal by O_3 and OH in the atmosphere. *Atmos. Environ.* **2005**, *39*, 3355−3367.

(21) Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kojima, E.; Kitamura, A.; Shimohigoshi, M.; Watanabe, T. Light-induced amphiphilic surfaces. *Nature* **1997**, *388*, 431−432.

(22) Fujishima, A.; Rao, T. N.; Tryk, D. A. Titanium dioxide photocatalysis. *J. Photochem. Photobiol., C: Photochem. Rev.* **2000**, *1*, 1−21.

(23) Guan, K. H. Relationship between photocatalytic activity, hydrophilicity and self-cleaning effect of TiO_2/SiO_2 films. *Surf. Coat. Technol.* **2005**, *191*, 155−160.

(24) Meites, L., Ed. *Handbook of Analytical. Chemistry*; McGraw−Hill: New York, 1963.

(25) Zhang, F.-S.; Nriagu, J. O.; Itoh, H. Photocatalytic removal and recovery of mercury from water using TiO_2-modified sewage sludge carbon. *J. Photochem. Photobiol., A: Chem.* **2004**, *167*, 223−228.

Received for review May 22, 2006. Revised manuscript received July 31, 2006. Accepted August 3, 2006.

ES061228A