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Short communication

# Removal of gaseous pollutants with a UV-$C_{254+185\,nm}$/$TiO_2$ irradiation system coupled with an air washer

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## Abstract

The water-insoluble gaseous pollutants NOx (NO and $NO_2$) and toluene were subjected to UV-$C_{254+185\,nm}$ irradiation in humid air, and their photodegradation was quantitatively studied. The pollutants were efficiently decomposed by the ozone and OH radicals produced by UV-$C_{254+185\,nm}$ irradiation. Because the decomposition products were water soluble, they could be removed with an air washer, which was used for post-treatment. When the photoreactor was dip-coated with a $TiO_2$ catalyst, the photodegradation of the pollutants was enhanced. We propose that the coupling of UV-$C_{254+185\,nm}$ irradiation and an air washer would be a useful system for the removal of gaseous pollutants.

*Keywords:* NOx; Toluene; $TiO_2$; Photodegradation; Decomposition products; Air washer

## 1. Introduction

In clean-room semiconductor manufacturing, various gaseous pollutants, such as sulfur dioxide ($SO_2$), nitrogen oxides (NOx), ammonia ($NH_3$), and volatile organic compounds (VOCs), are known to fatally damage fabricated wafers, electrical components, and other equipment [1]. The chemical adsorbents used to remove a wide range of gaseous pollutants are expensive, have an unpredictable life span, and require additional disposal or handling steps [2]. Therefore, demand for a more cost effective and efficient air-purification system is great.

Air washers, which are widely used to adjust indoor humidity in clean rooms, have recently received considerable attention for removing gaseous pollutants. An air washer can effectively remove water-soluble pollutants such as $SO_2$ and $NH_3$ by means of a fine mist sprayed through a nozzle, but water-insoluble pollutants are difficult to remove. However, converting water-insoluble pollutants into water-soluble materials would increase the number of gaseous pollutants that could be removed with an air washer.

This study describes an irradiation process that uses a UV-C lamp that emits 254- and 185-nm wavelengths (UV-$C_{254+185\,nm}$) to convert water-insoluble pollutants to water-soluble materials or to harmless substances. When humid air is irradiated with UV-$C_{254+185\,nm}$, large quantities of ozone and hydroxyl radicals are produced in the air stream [3,4]. In previous studies, we have reported that UV-$C_{254+185\,nm}$ irradiation efficiently decomposes some aromatic organic compounds to $CO_2$ and/or converts them into more water-soluble products such as aldehydes or carboxylic acids [5,6].

In this study, we chose water-insoluble NOx (NO and $NO_2$) and toluene as the target pollutants. We quantified the photodegradations arising from UV-$C_{254+185\,nm}$ irradiation and investigated the water-solubility of the decomposition products. A laboratory-scale air washer was used for post-treatment of the water-soluble decomposition products. We examined the possibility of enhancing the photodegradation of the pollutants by carrying out the UV-$C_{254+185\,nm}$ irradiation in a reactor dip-coated with $TiO_2$.

## 2. Materials and methods

Fig. 1 shows a schematic diagram of the experimental apparatus. The cylindrical photoreactor ($V = 0.55$ L) has five inner

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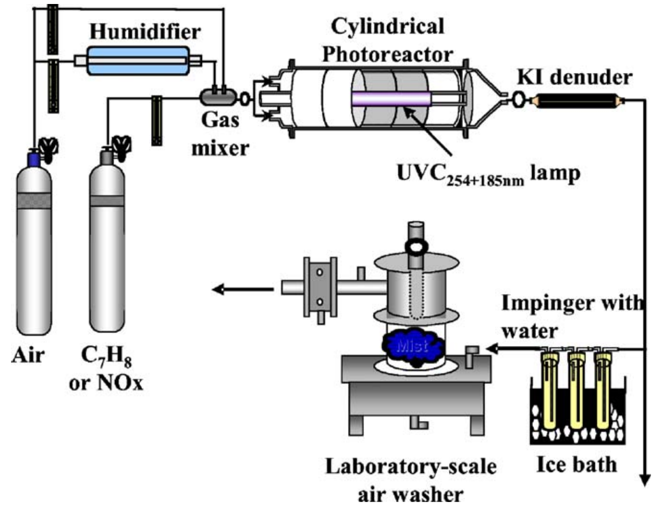

Fig. 1. Schematic diagram of experimental apparatus.

cylinders. In some of the reactions, a $TiO_2$ catalyst (Degussa P25) was used with UV irradiation to enhance the photodegradation. A sonicated mixture of 5 g of the $TiO_2$ catalyst in 300 mL of deionized water was dip-coated onto the innermost three cylinders of the photoreactor, and the cylinders were dried at 150 °C for 2 h in an oven. The dipping procedure was repeated four times, and then the cylinders were dried at 150 °C for 24 h. After the dipping procedure, the $TiO_2$ catalyst load on the insides of the cylinders was approximately 40 mg (ca. 0.15 mg cm$^{-2}$). The UV lamp was located at the center of the reactor. An ozone-producing low-pressure mercury lamp (GLZ4, Sankyo denki, Tokyo) with a maximum emission at 254 nm and a minor emission (ca. 5%) at 185 nm was used for irradiation. A laboratory-scale air washer with one water-spraying nozzle was used. Deionized water from the water tank (25 L) was sprayed (spray flow rate, 25 mL/min; spray pressure, 4 kg/cm) into the effluent gas stream emitted from the photoreactor. The mist was recirculated into the water tank.

The NOx or toluene gas was introduced into the photoreactor at a flow rate of 3 L/min and a relative humidity of ca. 40%. After the inlet and outlet concentrations reached equilibrium, the UV lamp was turned on. The removal ratios for the pollutants were calculated from the concentrations of the pollutants before and after UV-C$_{254+185\,nm}$ irradiation, and mass balance was established by quantifying the decomposition products. We measured the quantities of $CO_2$ and water-soluble organic intermediates (WSOI) obtained from toluene degradation and the quantities of $NO_2$ or $HNO_3$ obtained from NOx degradation.

The $HNO_3$ and WSOI selectivities were determined from the quantities collected in a series of three impingers containing pure water. The air-flow rate ranged from 0.8 to 1.0 L/min and the total sampled gas volume was 20 L for $HNO_3$ and 150 L for WSOI. The impingers were maintained at 5 °C to increase collection efficiency during sampling.

The toluene gas was monitored with a gas chromatograph (GC-14B, Shimadzu, Kyoto) equipped with a gas autosampler and a flame ionization detector. Carbon dioxide ($CO_2$) and carbon monoxide (CO) in the effluent gas were analyzed with a gas chromatograph (GC-15A, Shimadzu, Kyoto) equipped with a methane converter (MT-221, GL Science, Tokyo) and a flame ionization detector. A total organic compounds (TOC) analyzer (TOC-5000, Shimadzu, Kyoto) was used to quantify the total organic intermediates collected in the water.

NO and $NO_2$ were separately monitored with a chemiluminescence NOx analyzer. The liquid samples obtained from the impingers and the air washer were analyzed for $HNO_2$ and $HNO_3$ by means of an anion chromatograph (DX-100, Dionex, USA) equipped with an electroconductivity detector. The NOx analyzer could read $HNO_3$ as $NO_2$ because the analyzer contains a reduction catalyst capable of converting $HNO_3$ into NO. Thus, the $NO_2$ concentration obtained from the NOx analyzer was the sum of the $NO_2$ and $HNO_3$ concentrations. The NOx analyzer's conversion efficiency for $HNO_3$, obtained by means of a calibration test using standard gaseous $HNO_3$, was 85–90%.

Ozone in the effluent gas was removed with a potassium iodide (KI)-coated annular denuder [7] because ozone could introduce experimental error as well as seriously damage the GC column.

## 3. Results and discussion

### 3.1. Trapping efficiency of the air washer

In a preliminary test, the trapping efficiencies of the air washer (AW) for water-insoluble NO, $NO_2$, toluene, and water-soluble $HNO_3$ were examined. The water-soluble $HNO_3$ was completely trapped (>99%) at the concentration range and flow rates tested, owing to its high water solubility. In contrast, less than 5% of the water-insoluble NO, $NO_2$, and toluene were trapped. Therefore, the water-insoluble pollutants had to be converted into water-soluble materials by means of a pre-treatment procedure in order to be removed by the AW.

### 3.2. Photodegradation of NOx and toluene with UV-C$_{254+185\,nm}$ irradiation and the water solubility of decomposition products

UV-C$_{254+185\,nm}$ completely oxidized NO gas to $HNO_3$ (>ca. 90%) and $NO_2$ (<ca. 10%) (Table 1). $NO_2$ gas was almost completely oxidized (ca. 90%) by irradiation and was converted almost completely to $HNO_3$.

UV-C$_{254+185\,nm}$ irradiation of humid air simultaneously produces abundant $O_3$ and OH radicals via photochemical reaction. Upon entering the UV-irradiated air, NO reacts rapidly with $O_3$ to form $NO_2$ (Eq. (1)), and then $NO_2$ is readily oxidized to $HNO_3$

Table 1
Removal ratios of NOx and toluene and product selectivity after UV irradiation[a]

| | Removal ratio (%) | Product selectivity (%) |
|---|---|---|
| NO | 100 | $HNO_3$ (91), $NO_2$ (9) |
| $NO_2$ | 92 | $HNO_3$ (100) |
| $C_7H_8$ | 60 | $CO_2$ (62), CO (8), WSOI[b] (25), unknown (5) |

[a] $[NOx]_0$, $[C_7H_8]_0$ = ca. 0.6 ppm; RT, 11 s (3 L/min); RH, ca. 40%.
[b] WSOI, water-soluble organic intermediates.

in the presence of OH radicals (Eq. (2)). In addition, $NO_2$ gas also reacts directly with OH radicals.

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{1}$$

$$NO_2 + OH + M \rightarrow HNO_3 + M\,(M = O_2 \text{ or } N_2) \tag{2}$$

Therefore, it is reasonable to expect the combination of ozone and OH radicals to be very useful for converting NOx into $HNO_3$. Methods that can simultaneously produce large quantities of $O_3$ and OH radicals are rare. A corona discharge technique was recently used to effectively produce ozone and OH radicals, but the energy efficiency of the technique is low, and undesirable by-products are produced [8].

The removal ratio for the photodegradation of toluene was moderate compared to that for NOx, owing to toluene's lower reactivity with OH radicals. Nevertheless, the organic intermediates that formed were water-soluble compounds that could be collected efficiently with water, which implies that the intermediates can be washed out by a gas washing technique, such as an air washer.

### 3.3. *Treatment of NOx and toluene with the UV-C$_{254+185\,nm}$ irradiation system and the air washer*

When NO and $NO_2$ were subjected to UV-C$_{254+185\,nm}$ irradiation, the NO concentration dropped rapidly to zero and the $NO_2$ concentration increased (Fig. 2). As the reaction proceeded, the $NO_2$ concentration slowly increased, reaching a steady state after 400 min (7 h). The time course of the $NO_2$ concentration is thought to arise from the fact that the NOx analyzer counts $HNO_3$ as $NO_2$. In this initial stage, $HNO_3$ is thought to be strongly adsorbed on the wall of the photoreactor and venting line, so the $NO_2$ value was low. As the adsorption of $HNO_3$ decreased, the $NO_2$ concentration increased, and when the adsorption–desorption of $HNO_3$ reached equilibrium, the $NO_2$ value stabilized at its highest value. Note, however, that in this equilibrium state, the $NO_2$ value did not reach the initial concentration of NO. This result can be explained by the reduction ratio of $HNO_3$ in the NOx analyzer, as mentioned in Section 2.

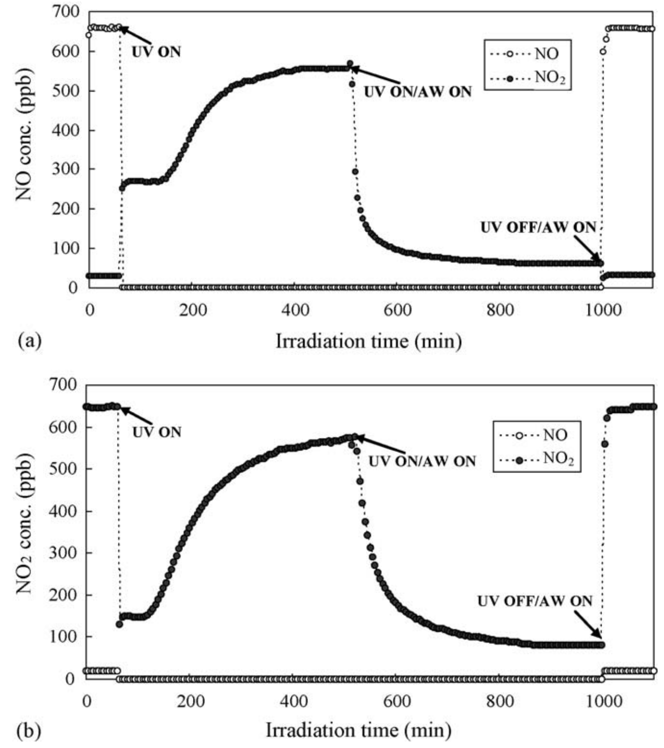

Fig. 2. (a) Time course of NO concentration upon treatment with UV irradiation and the AW. $[NO]_0$, ca. 0.65 ppm; RT, 11 s (3 L/min); RH, ca. 40%. (b) Time course of $NO_2$ concentration upon treatment with UV irradiation and the AW. $[NO_2]_0$, ca. 0.65 ppm; RT, 11 s (3 L/min); RH, ca. 40%.

When the effluent gas containing $HNO_3$ was passed through the AW, the $NO_2$ concentration rapidly dropped and reached a new, lower equilibrium value, since $HNO_3$ was trapped in the AW. The time course of the photodegradation of $NO_2$ was similar to that of NO. To confirm the trapping ability of the AW, we continuously analyzed the $HNO_3$ concentration in the trap water during the operation (Fig. 3) and found that the $HNO_3$ concentration in the water increased with time, indicating that $HNO_3$ was actually trapped by the mist.

The trapping efficiency for the WSOI of toluene in the effluent gas by means of the AW (Fig. 4) indicated that the quantity of organic intermediates collected in the water was apparently reduced after passing through the AW, implying that they were trapped in the AW.

These results clearly indicate that UV pre-treatment for water-insoluble pollutants effectively degraded them and converted them to water-soluble materials that could be easily removed by the AW.

### 3.4. *Efficacy of TiO$_2$ use under UV-C$_{254+185\,nm}$ irradiation*

To enhance the photodegradation of NOx and toluene, we used $TiO_2$ in combination with UV-C$_{254+185\,nm}$ irradiation. Using $TiO_2$ enhanced the removal of $NO_2$ and toluene under

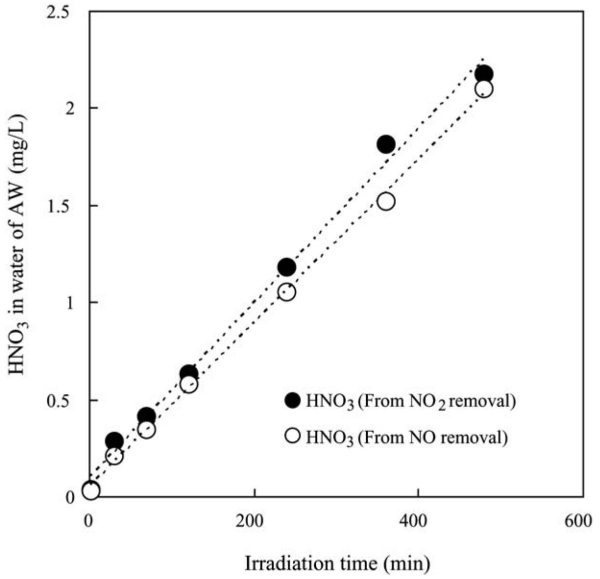

Fig. 3. Time dependence of the $HNO_3$ concentration in the trap water of the AW.

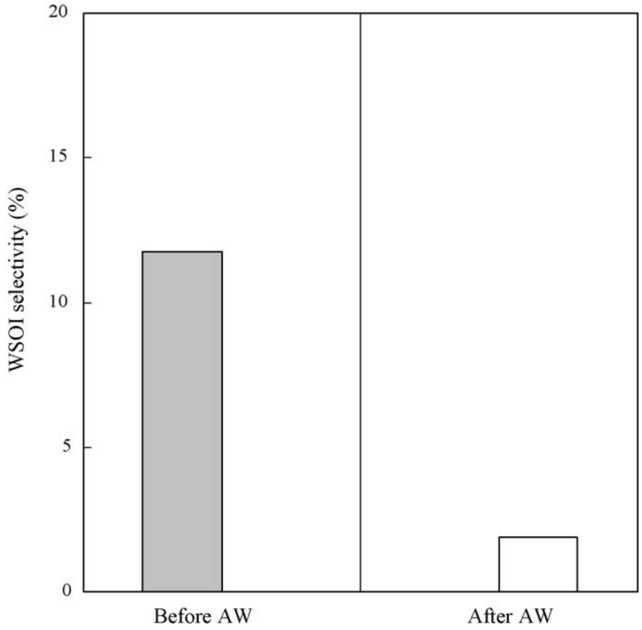

Fig. 4. WSOI selectivity of toluene decomposition, before and after passage through the AW. $[C_7H_8]_0$, 0.6 ppm; RH, ca. 40%; RT, 33 s (3 L/min).

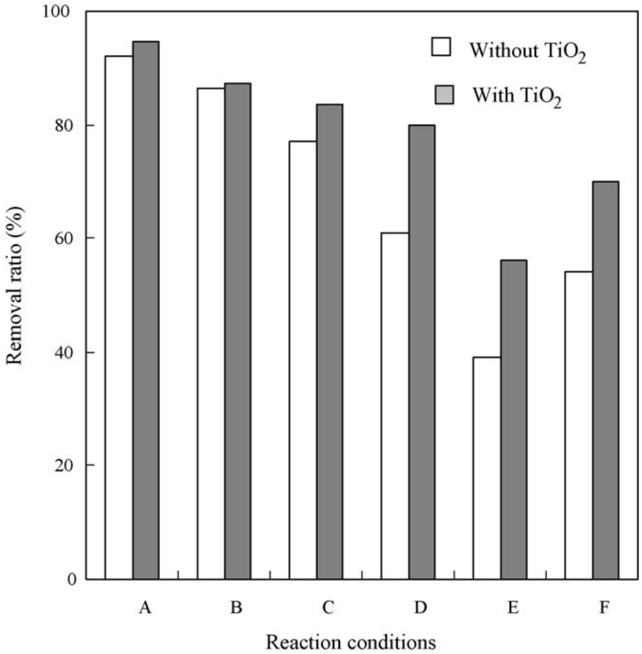

Fig. 5. Effect of $TiO_2$ on the UV-$C_{254+185\,nm}$ irradiation of $NO_2$ and toluene. A: $[NO_2]_0$, 0.6 ppm; RT, 11 s (3 L/min). B: $[NO_2]_0$, 10 ppm; RT, 11 s (3 L/min). C: $[NO_2]_0$, 0.6 ppm; RT, 6.6 s (5 L/min). D: $[C_7H_8]_0$, 0.6 ppm; RT, 11 s (3 L/min). E: $[C_7H_8]_0$, 10 ppm; RT, 11 s (3 L/min). F: $[C_7H_8]_0$, 0.6 ppm; RT, 6.6 s (5 L/min). RH, ca. 40%.

all reaction conditions (Fig. 5). We supposed that the enhancement was responsible for the photocatalytic oxidation power of $TiO_2$. In previous studies, we have reported some of the advantages of combining $TiO_2$ and UV-$C_{254+185\,nm}$ irradiation, such as increased water solubility of organic intermediates, prevention of catalyst deactivation, and inhibited formation of undesirable by-products [6,9].

## 4. Conclusions

A useful process for the degradation of NOx and toluene by means of UV-$C_{254+185\,nm}$/$TiO_2$ irradiation coupled with the use of an air washer was presented. The OH radicals and ozone produced by UV-$C_{254+185\,nm}$ irradiation effectively degraded NOx and toluene to $HNO_3$ and $CO_2$, respectively. The organic intermediates formed during toluene degradation were highly water soluble and could therefore be effectively removed, along with the $HNO_3$, by the air washer. The use of $TiO_2$ along with the UV-$C_{254+185\,nm}$ irradiation increased the photodegradation of pollutants by means of photocatalytic oxidation.

We propose that the combination of UV-C/$TiO_2$ treatment and an air washer is a useful process for effectively removing gaseous pollutants from the air, particularly those with high reactivity with OH radicals and ozone.

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