Verification of High-density Hydroxyl Radical Generating Technology and Relevant Application Technology of Free Radical

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Chapter One - Introduction

Hydroxyl radical (•OH) is one of the important reactive species in the advanced oxidation process. It has an unpaired electron on an open shell configuration, and has a covalent bond. Two electrons are respectively from oxygen atom and hydrogen atom as it shows in the figure 1-1. The hydroxyl radical is highly reactive and short-lived. It forms an important part of radical chemistry. Most notably hydroxyl radical is produced from the decomposition of hydro-peroxides (ROOH) or, the reaction of excited atomic oxygen with water vapor in atmospheric chemistry. One of the most famous is Fenton reaction. H.J.H Fenton discovered in 1894 that several metals have a special oxygen transfer properties which improve the use of hydrogen peroxide. Actually, some metals have a strong catalytic power to generate highly reactive hydroxyl radical (•OH). Fenton's reagent is a solution of hydrogen peroxide and an iron catalyst. Iron (II) sulfate is a typical iron compound in Fenton's reagent. Since this discovery, the iron catalyzed hydrogen peroxide has been called Fenton's reaction. Hydrogen peroxide reacts with ferrous iron (II) to form ferric iron (II) complex that subsequently reacts to form hydroxyl radicals. It generates some hydroxyl radical as it shows in the following equations:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$$

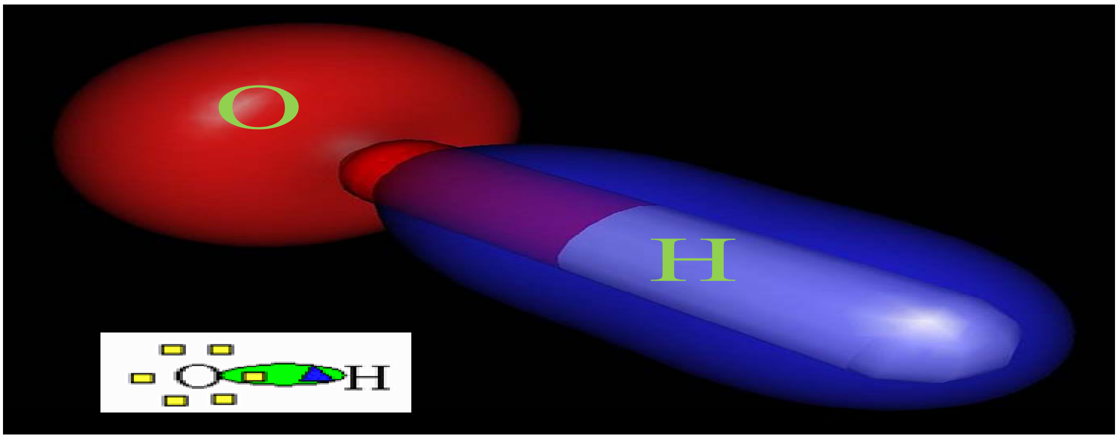


Figure 1-1 Molecular orbital of the hydroxyl radical with unpaired electro

In the atmosphere, the hydroxyl radical is often referred to as the "detergent", and it plays a central role in the oxidation and removal of many atmospheric compounds, because it reacts with many pollutants, often acting as the first step to their removal. Its major source in the troposphere is the reaction of electronically excited atomic oxygen with water vapor, and excited atomic oxygen is produced from UV-photolysis of ozone. Now, the most powerful advanced oxidation systems are based on the generation of hydroxyl radical, and the oxidation rate is strongly dependent on hydroxyl radical concentration. Most of the hydroxyl radical is produced from ozone in chain reaction where alkali or hydrogen peroxide acts as initiator. Table 1-1 lists some typical hydroxyl radical generation systems.

Table 1-1 List of typical hydroxyl radical generation systems

Non-photochemical	Photochemical
O_3 at elevated pH (>8.5)	O_3/UV
O_3/US	O_3/H_2O_2/UV
O_3/AC (activated carbon)	H_2O_2/UV
O_3/H_2O_2/US	H_2O_2/Fe^{2+}/UV (photo-Fenton)
H_2O/US	H_2O/UV/TiO_2
H_2O_2/US	H_2O_2/UV/TiO_2
Fe^{2+}/H_2O_2 (Fenton system)	O_3/UV/TiO_2
Electro-Fenton	H_2O/UV/US
Pulsed plasma	Vacuum UV
Microwave	
Wet air oxidation	
Supercritical water oxidation	

*Annex: Ultraviolet (UV); Ultrasonic (US).

In general, the effectiveness of an Advanced Oxidation Processes is proportional to its ability to generate hydroxyl radicals. Methods such ozonation, hydrogen peroxide and/or UV light may have mechanisms for destroying organic contaminants which involve formation of hydroxyl radicals. When O_3 and H_2O_2 are simultaneously added to water, they participate in a complex chain of reactions that result in the formation of radicals such as the hydroxyl radical ($\cdot OH$) and the superoxide radical ($\cdot O_2$). H_2O_2 enhances the transformation of O_3 to $\cdot OH$ in solution and as a result this treatment is more effective than either ozonation or hydrogen peroxide alone. Meanwhile, the generation of radical can be enhanced by using ultraviolet (UV) radiation, which induces formation of free radicals. Ultraviolet irradiation can be used together with ozone (O_3/UV) or hydrogen peroxide (UV/H_2O_2). And if we add the ultrasonic, the effectiveness of an Advanced Oxidation Processes will intensify. Now, the generation of radical using a combination of ultraviolet irradiation catalyzed with TiO_2 is based on the illumination of the titanium dioxide (which is a semiconductor) with ultraviolet light. This results the excitation of its valence band electrons to the conduction band and the formation of holes. Adsorbed water molecules and ozone take part in the reaction of producing hydroxyl radicals, while superoxide anion radical (•O_2) is also generated.

The hydroxyl radical has a very short live in vivo half-life of approx. 10^{-9}s and a high reactivity. It is an extremely powerful and non-selective oxidation agent, second only to Fluorine in power. This makes it be a very dangerous compound to the organism. Unlike superoxide, which can be detoxified by superoxide dismutase, the hydroxyl radical cannot be eliminated by an enzymatic reaction. It can damage virtually all types of macromolecules: carbohydrates, nucleic acids (mutations), lipids (lipid peroxidation) and amino acids (e.g. conversion of Phe to m-Tyrosine and o-Tyrosine) through this chain reaction. The reaction will continue until it is ultimately quenched. The only means to protect important cellular structures is the use of antioxidants such as glutathione and of effective repair systems. Antioxidants are widely used in dietary supplements and have been investigated for the prevention of diseases such as cancer, coronary heart disease and even altitude sickness. In addition hydroxyl radical oxidation potential is very strong, so it is stronger oxidizing agents than ozone and hypochlorous acid, and can oxidize the organic material is faster than using ozone and hypochlorous acid. It is known that ozone and hypochlorous acid are applied in waste-water treatment. Although fluorine gas has a higher electronegative oxidation potential, it is not used in water treatment. Following is a listing of common chemical oxidants, placed in the order of their oxidizing strength:

Table 1-2 Relative power of chemical oxidants

Species	Formula	Oxidation Potential, (electron-volt)
Fluorine	F	3.06
Hydroxyl Radical	•OH	2.85
Sulfate Radical	•SO_4^-	2.60
Excited Atomic Oxygen	O_1	2.42
Ozone	O_3	2.07
Hydrogen Peroxide	H_2O_2	1.77
Perhydroxyl Radical	HO_2	1.70
Hypochlorous Acid	HClO	1.49
Chlorine	Cl_2	1.36
Hypobromou Acid	HBrO	1.33
Oxygen	O_2	1.23
Chlorine Dioxide	ClO_2	0.95

This comparison shows that oxidation can be achieved by using compounds which have higher oxidation potentials (Eo) than that of oxygen (1.23V) in general. The difference of the oxidation potential over the potential of oxygen is a measure of the oxidative capability of oxidizing agents, and with the higher the oxidation potential, oxidative capability is stronger. This comparison also shows that hydroxyl radical has unmatched capability of oxidative treatment. The only oxidant with even higher potential is fluorine, with its oxidation potential of Eo = 2.85 V, while ozone and hypochlorous acid have the oxidation potential of only 2.07V and 1.49V.

Hydroxyl radical is an ultimate oxidation tool — able to attack any molecule in their vicinity in order to balance their unpaired electron configuration. It can cut the organic C-C bond, and break double bonds (such as C=C, C=O, N=N and so on), degrade hydrocarbons, cause epoxidation and aromatic ring opening, radical polymerization, formation of secondary radicals and many other types of reactions. It is shown such as figure 1-2. So, utilizing the strong oxidizing strength of hydroxyl radical, oxidation reaction is the most effective way of degrading and eliminating all kinds of pollutants and waste chemicals both in air and water. It is also one of the basic tools in a variety of chemical reactions and processes.

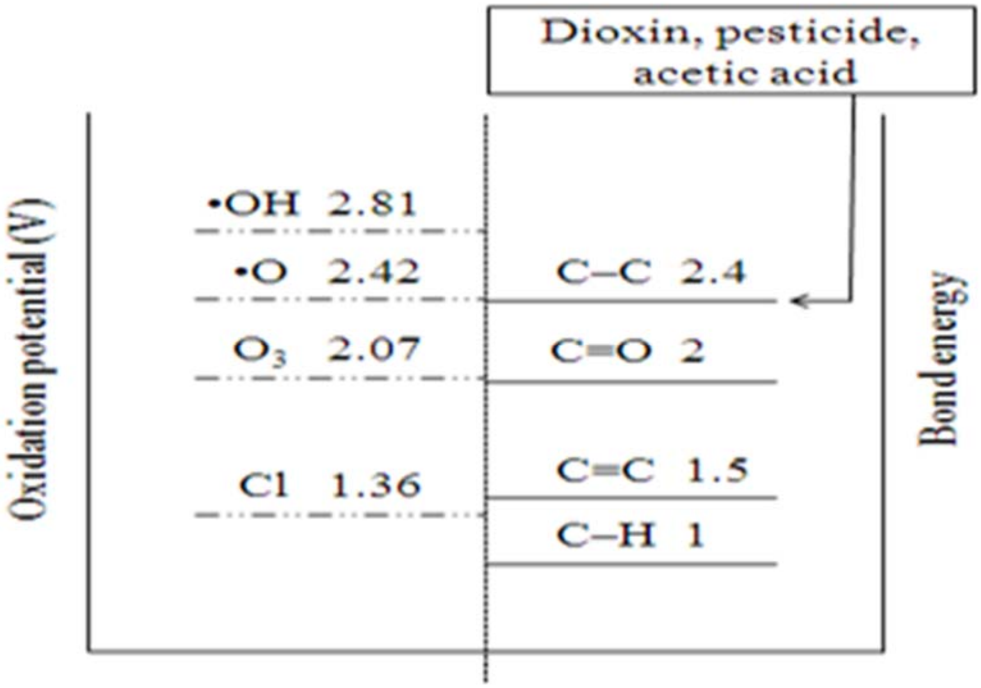


Figure 1-1 Cause of degrading and eliminating all kinds of organic matter using hydroxyl radical

Advanced oxidation process (AOP) is based on techniques of generation of highly reactive species (especially the hydroxyl radical) that are able to react with a range of compound, even with chemicals that are otherwise very difficult to degrade. The degradation reaction is initiated by the radical proceeds until thermodynamically stable oxidation products are formed. Meanwhile the end products of complete oxidation of organic compounds are carbon dioxide (CO_2) and water (H_2O). It is shown such as figure 1-3.

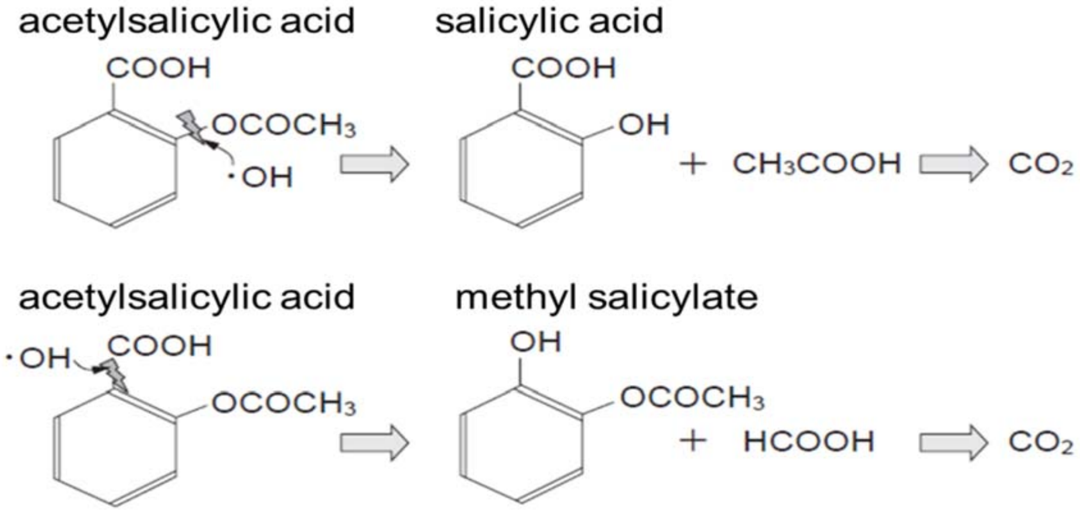


Figure 1-3 End products of complete oxidation of organic compounds reacting with hydroxyl radical

Advanced Oxidation process is an environmentally friendly approach to target pollutants and contaminants, such as in air and waste water, to remove toxic or non-degradable materials. AOP deals with the removal of aromatics, pesticides, petroleum constituents, volatile organic compounds (VOC), petroleum hydrocarbons and chlorinated hydrocarbons, dyes and organic matter.

In recent years demand has been increasing for effectively disinfect, deodorize, air purification, water treatment, wafer rinse containing metal impurities such as Ag, Ni or Al, and recalcitrant organic matter such as dioxins or agricultural chemicals, which has not been able to be treated by traditional treatment techniques using chlorine or ozone. The hydroxyl radical is conventionally generated by the reaction of dissolved ozone. Hydrogen peroxide or ultraviolet light is used for decomposition of the dissolved ozone. However, the hydroxyl radical production efficiency of the conventional method is not high, as one hydroxyl radical is produced from three molecules of ozone. And as it is short live, it is difficult to capture and determination. Detection methods require high sensitivity and high selectivity. Although most techniques are suitable for certain experimental objectives, they all have limitations, and need high cost and complicated operation. For these reasons, a high-efficiency hydroxyl radical generation technique and a highly efficient and convenient semi-quantitative and qualitative system of hydroxyl radical are desired. In our laboratory, we established the system which was an ozone/ultrasonic/ultraviolet rays/photocatalyst unit, and every event was used by alone or in combination to try decomposition and detoxification of various environmental pollutants.

In this paper, chapter two analyzes photodecomposition behaviors of pesticides in the source for water supply using an alumina carrier-titanium dioxide photocatalyst. Chapter three will introduce novel hydroxyl radical generation technology. In order to largely promote hydroxyl radical generating efficiency, the technology is developed which comprehensively uses ozone, ultraviolet illuminating, low-megahertz ultrasonic and titania nanotube photocatalyst, meanwhile adopts the method of high velocity impact of forging thermal spraying. Chapter four analyzes photo-decomposition of volatile organic compound using nano-reaction field separation TiO_2 photocatalyst. Chapter five discusses production of active intermediates and decomposition behaviours and effects of organic compounds using hydroxyl radical in the ultraviolet ray/supersonic wave multiple reactions with TiO_2 photocatalyst. Most of those organic compounds are difficult to be decomposed by ozone and chlorine. Chapter six discusses the generation of hydroxyl radical in the process of ozone/ultraviolet ray/supersonic wave multiple reactions with TiO_2 photocatalyst, and quantitative and qualitative analysis of generated hydroxyl radical with chemiluminescence and other methods. Chapter seven discusses contaminants cleaning and decomposition effects using hydroxyl radical water. For all of the electronic elements, cleaning technology is exactly requisite in the process of producing. Recent years, chemical cleaning drugs were gradually prohibited, and hydroxyl radical is attracting more and more attention, which is expected to function in dealing with those stable metal impurities that are difficult to be decomposed by ozone and chlorine. Chapter eight summarizes the paper, points out the innovation, future application and the deficiency of the study in the end.

In addition, when the shortage of surface water resources is becoming growing, groundwater usage has increased year by year. Over the past 30 years, many countries have found that groundwater and soil were polluted by pesticide and heavy metals, and these kinds of pollution are difficult to eliminate. Especially in China, excessive use of pesticide and chemical fertilizer as well as pesticide product's structure is irrational, result in about 70% of the pesticide scattering into the environment. Then because residual pesticide which is in the soil permeates into the groundwater, groundwater and soil are polluted by pesticide. In addition, residual pesticide and trace heavy metals are detected with relatively high frequency in fresh fruits, fresh vegetables, and frozen food. In China in recent years, as people focus on food safety and health, the awareness of groundwater and soil pollution prevention has been greatly improved. Hydroxyl radical is strong oxidizing agent. Now it is increasingly expected to treat decompose organic pollutant (including pesticide) which is difficult to be treated by ozone and chlorine. According to the advanced oxidation process, pesticide pollution of groundwater and soil can be eliminated by hydroxyl radical. Using ozone, ultrasonic, ultraviolet rays and photocatalyst with together, it can generate high concentration of hydroxyl radical, and it is earth-friendly. Meanwhile, we can calcium polysulfide (CaSx) as insolubilization treatment material to remove heavy metals ions in wastewater and sediment/soil treatment. Others, it will be considered that hydroxyl radical be also applied in some fields such as food sterilization, medical relationship and clothing relationship.

Chapter Two - Photodecomposition behaviors of pesticides in the source for water supply using an alumina carrier-titanium dioxide photocatalyst

2.1 Introduction

The countermeasures against toxic substances or musty odor cause substances in the source for water supply have become a serious subject with the pollution of environmental waters. For the purpose of the utilization of the photodecomposition method for the water purification at a water purification plant or a water purifier, we have investigated on the photodecomposition behaviors of organic pollutants, total organic compounds, formaldehyde, total organic halides, trihalomethanes, geosmin and 2-methyl-iso-borneol using a titanium dioxide photocatalyst. Relatively high photodecomposition efficiencies were obtained for these substances.

Pesticide is one of the toxic chemical substances polluting the source for water supply, vegetables, fruits, etc. Then, the residual pesticides in many kinds of food have already been regulated and the aiming standard values of 101 types of pesticide for tap water quality control were set up in 2003. However, only 21 in 117 types of pesticide showed over 80% of removal ratio in the coagulation and sedimentation usually performed at a water purification plant. Then, we investigated on the photodecomposition behaviors of the 5 types of pesticide which were largely used in Kitakyushu district.

We have ever used silica gel having high decomposition efficiency as a carrier of TiO_2 photocatalyst. However, a silica gel carrier was fragile. In addition, sufficient endurance of the carrier is demanded when the decomposition of chemicals in water and food or that disinfection using supersonic wave together is performed. Then, we also investigated on the photodecomposition ability with an alumina carrier, which could stand against ultra violet (UV) light and water, instead of silica gel carrier.

2.2 Material and methods

2.2.1 Instruments

Gas chromatograph/mass spectrometer (GC/MS) was a Hewlett Packard HP-5890 series and a JEOL auto mass system. Total nitrogen (T-N) analysis was performed using a Tokyo Kasei Ind. Co. TCI-NOX 1000, GASTORR GT-102, VISIBLE DETECTOR S-3250 and AUTO SAMPLER SS-3600, while other determinations were from Hitachi Co. U-2000A a spectrophotometer was used.

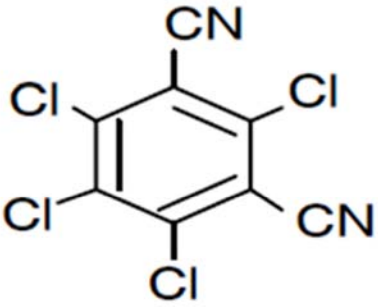
2.2.2 Objective pesticides and other reagents

Five pesticides that was shown as table 2-1 were selected for an objective pesticide. These pesticides were used in the Onga River Basin and their aiming standard values in tap water quality were established. Their structural formulas were shown in figure 1-1. Dinitrophenol (DNP) was used as a chemical substance for the capability evaluation of alumina carrier. These chemical substances were obtained from Hayashi Pure Chemical Industries, Wako Pure Chemical Industries and Tokyo Kasei Kogyo Co. Each standard solution was prepared by the dilution with acetone. An alumina carrier was obtained from Sumitomo Chemical Co. The properties of the alumina and silica gel carriers, comparative carriers, were shown in table 2-2. Two types of alumina are NK124 and NKHO24.

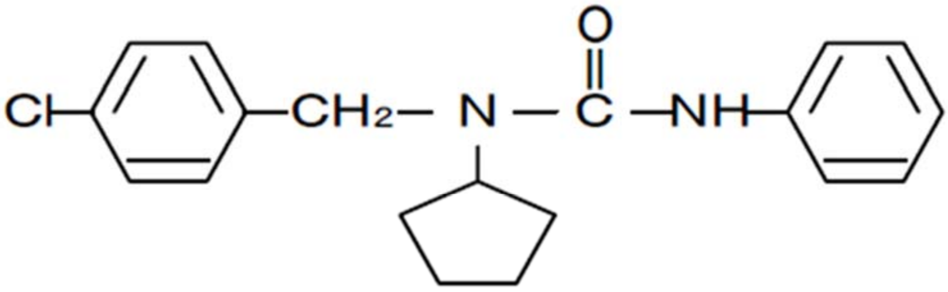
Table 2-1 Shipped amounts and the aiming water qualities of the objective pesticides in the Onga River Basin

Pesticide	Use	Shipped amount [a] (kg)	Aiming standard Value (mg/L)
Chlorthalonil	Disinfectant	185	0.05
Pencycuron	Disinfectant	686	0.04
Cafenstrole	Herbicide	1,946	0.008
Thiobencarb	Herbicide	155	0.02
Trifluralin	Herbicide	5,238	0.06

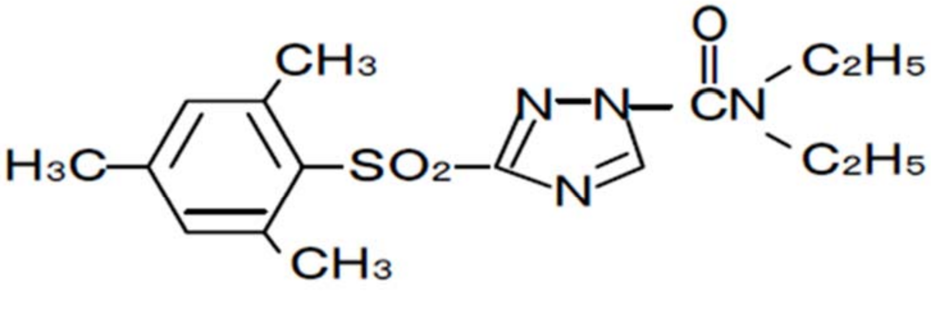
[a] The values in 2003



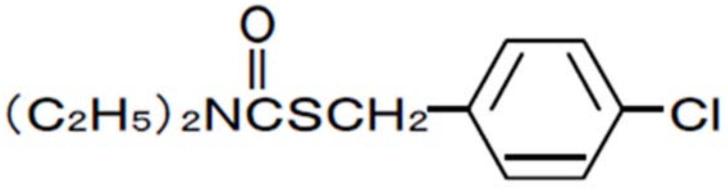
Chlorthalonil



Pencycuron



Cafenstrole



Thiobencarb

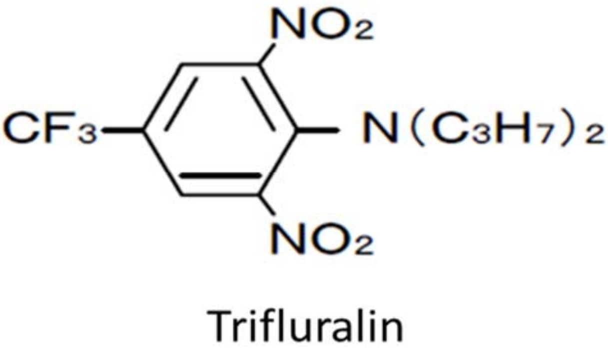


Figure 2-1 Structural formulas of the objective pesticides

Table 2-2 Properties of alumina and silica gel carriers

Item	Carrier		
	NK124	NKHO24	Silica gel
Particle size (mm)	2-4	2-4	1.7-4
Al_2O_3 contents (%)	99.9	99.7	—
Micropore volume (cm^3/g)	0.77	0.58	—
Relative surface area (m^2/g)	130	160	—
Compacting strength (kg)	2	6	—
Supporting ratio (%)	20	17	25

Two types of alumina are NK124 and NKHO24 are shown as figure 2-2. They and silica gel carrier-TiO_2 photocatalysts were produced by the Sol-Gel Method. All solvents were the grade reagents for pesticide residue analysis, which were obtained from Kanto Chemical Co. and Wako Pure Chemical Industries. Other reagents were special grade reagents, which were obtained from Wako Pure Chemical Industries. Anhydrous Na_2SO_4 and NaCl were heated at 800 °C for 3 h after acetone-washing. The water was purified using a Millipore Milli-Q Ultra-pure Water System.

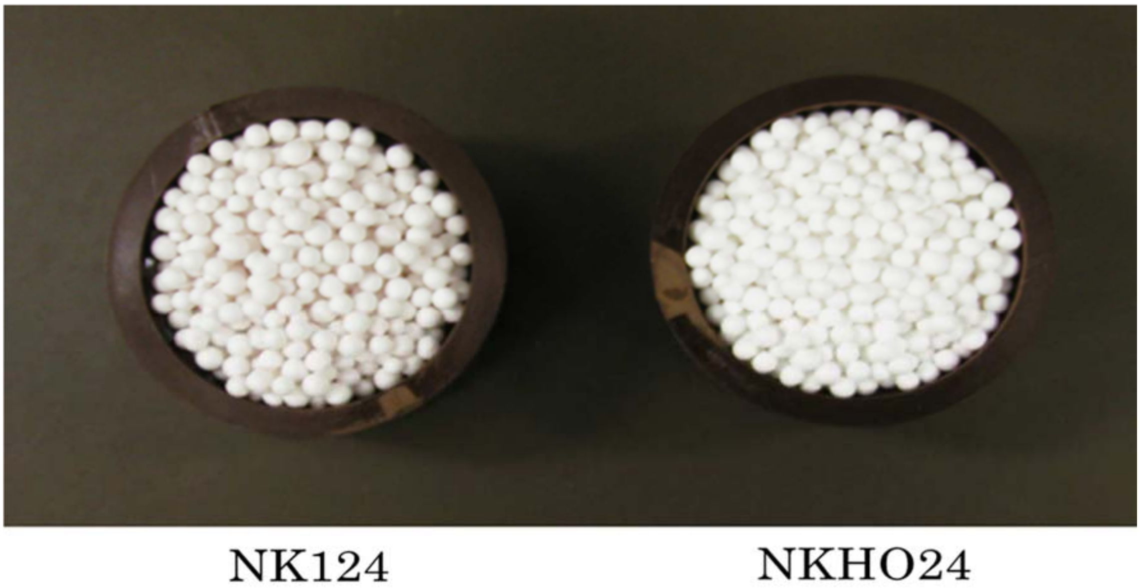


Figure 2-2 Prepared alumina carrier-TiO_2 photocatalysts

2.2.3 Apparatus for the photodecomposition of the pesticides

The apparatus for the photodecomposition experiments of the pesticides and DNP was shown in figure 2-3. The photo-reactor which was shown as figure 2-4 was made of stainless steel and equipped with a 6 W low pressure mercury lamp (a Matsushita Electric Ind. Co. GL6/Q) and a stabilizer (Nihon Fluorescence Electric Co.). Eighty five milliliters of each photocatalyst was packed in a thickness of about 5 mm. The UV illumination intensity on the surface of catalyst was 10 mW/cm^2. Sample water was circulated with a roller pump (Furue Science Co.).

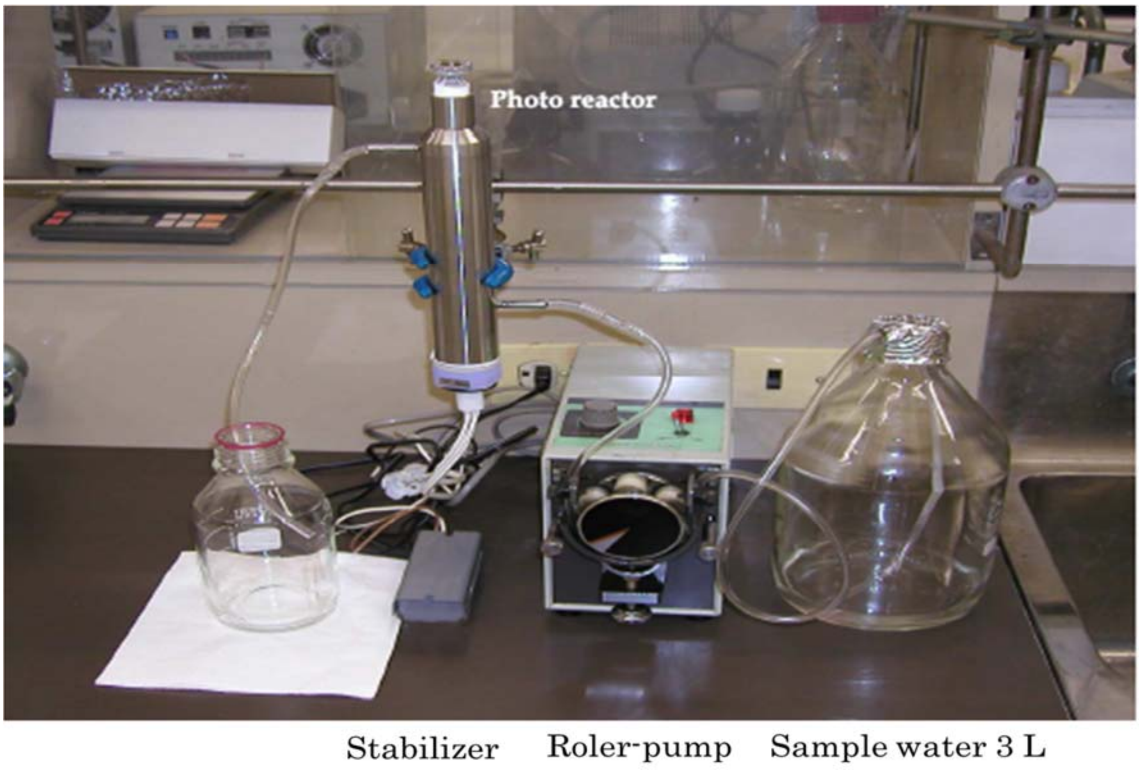


Figure 2-3 Apparatus for the photodecomposition of the pesticides

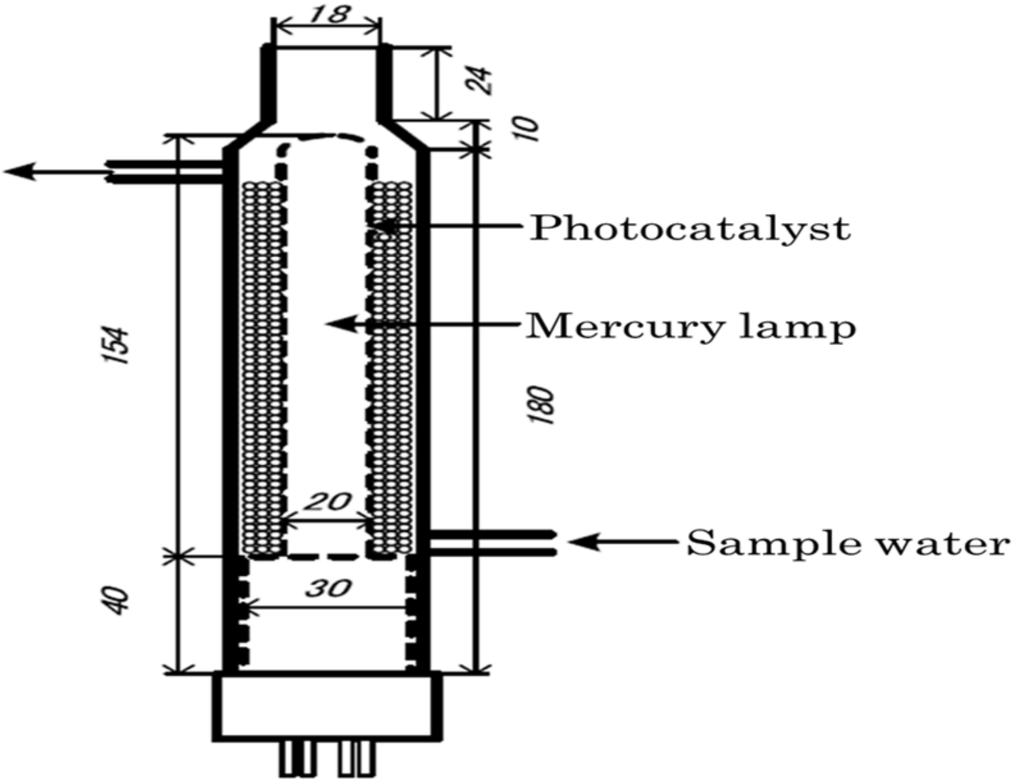


Figure 2-4 Structure of photoreactor

2.2.4 Analyses of pesticides, DNP and other items

The quantification of the pesticides and DNP in UV irradiated solution was performed in the next procedure. About 2 g of NaCl was added in 40 ml of UV irradiated solution and each pesticide or DNP was extracted with 4 ml of dichloromethane. The dichloromethane layer was separated from aqueous layer, dehydrated with anhydrous Na_2SO_4 and analysed by the GC/MS method. The GC/MS conditions were shown in table 2-3. Each calibration curve showed good linearity in the quantification range. Their recoveries by the method were over 85%.

PH, suspended solid matter (SS), BOD, KMnO4 consumption, total nitrogen (T-N), total phosphorus (T-P) and electric conductivity (EC) were measured by the method of Japanese Industrial Standard K0102.

Table 2-3 GC/MS conditions

Column	DB-5MS (5%Diphenyl 95%dimethyl polysiloxane) 0.25 mm × 30 m × 0.25 μm
Column temperature	60 °C (1 min)－30 °C min-1－130 °C－5 °C/min －240 °C－10 °C/min－300 °C (10 min)
Injector temperature	250 °C
Carrier gas	He1.5 mL/min
Transfer line temperature	260 °C
Mode	EI

2.2.5 The photodecomposition capability experiments of alumina carrier-TiO2 photocatalysts and photodecomposition experiments of pesticides

Each alumina or silica gel carrier-TiO_2 photocatalyst was packed in the photoreactor. The water samples for DNP and pesticides experiments were prepared by adding 3 ml of each 1,000 mg l-1 DNP or pesticide acetone solution in 3 l of purified water (for the photo-decomposition capability experiment of photocatalyst) or the river water (for the photodecomposition experiment of pesticide). Quality of the water was shown as table 2-4. The water sample was vigorously shaken for 30 min using a separatory funnel and placed in 5 l glass bottle. The water sample was firstly circulated for 30 min at l min-1 of flow rate by stirring and the system was allowed to reach equilibrium. Then the mercury lamp was switched on. The UV irradiated solution was periodically withdrawn during irradiation and DNP or each pesticide was quantified by the GC/MS method. The photodecomposition experiments of pesticides without a photocatalyst were also performed.

Table 2-4 Quality of the river water used for this experiment

Item	Concentration
pH	7.6
SS (mg/L)	6
BOD (mg/L)	3.5
$KMnO_4$ consumption (mg/L)	5.8
T-N (mg/L)	1.52
T-P (mg/L)	0.08
EC (μS/cm)	264

2.3 Results and discussion

2.3.1 Comparison of the photodecomposition capability of alumina carrier-TiO_2 photocatalysts

Figure 2-5 shows the photodecomposition rates of DNP using the alumina and silica gel carrier-TiO_2 photocatalysts. DNP was decreased exponentially with reaction time (t) and the rate of DNP disappearance was nearly represented by a first-order process. The values of pseudo-first-order rate constant (k: $C=C_0e^{-kt}$) of NK124, NKHO24 and silica gel carrier-TiO_2 photocatalysts determined from the plot of data points (C/C_0 vs. t) were 0.027, 0.016 and 0.030 min^{-1}, respectively. The rate constant of NK124 carrier-TiO_2 photocatalyst was near that of silica gel-TiO_2 photocatalyst. The micropore volume of NK124 is larger than that of NKHO24 but its relative surface area is smaller than that of NKHO24. The supporting ratio of NK124 was higher than that of NKHO24. It was supposed that the deference of DNP photodecomposition rate was caused by the deference of supporting ratio. Then, the photodecomposition experiments of the pesticides were performed using a NK124 carrier-TiO_2 photocatalyst.

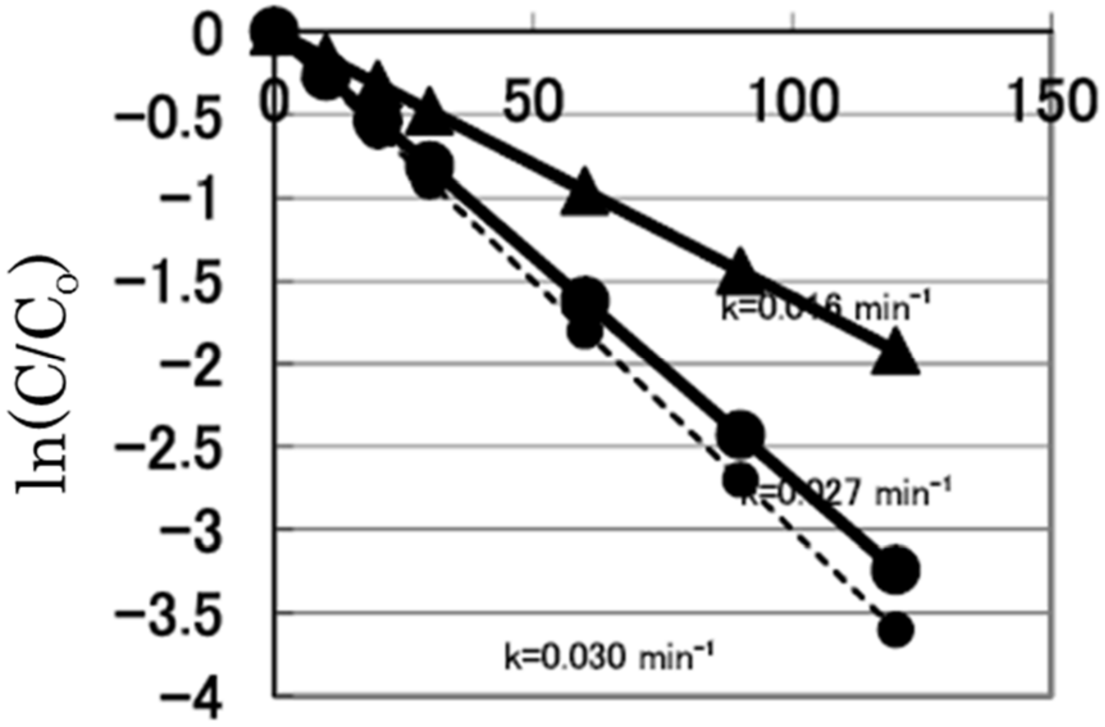


Figure 2-5 Photodecomposition rates of DNP

2.3.2 Photodecomposition behaviors of pesticides

From figure 2-6 to figure 2-10, they show the photodecomposition ratios of the pesticides. These pesticides were decomposed faster than DNP and the removal efficiencies after 3 min UV irradiation were 94% (Cafenstrole), 92% (Chlorthalonil), 75% (Thiobencarb), 67% (Pencycuron), 58% (Trifluralin) and 8% (DNP). After 30 min UV irradiation, the removal efficiencies of cafenstrole and chlorthalonil, and thiobencarb, pencycuron and trifluralin, were 98 and 94%, respectively. The UV illumination intensity in the experiments was so strong that the same removal efficiencies as with the photocatalyst were obtained without the photocatalyst.

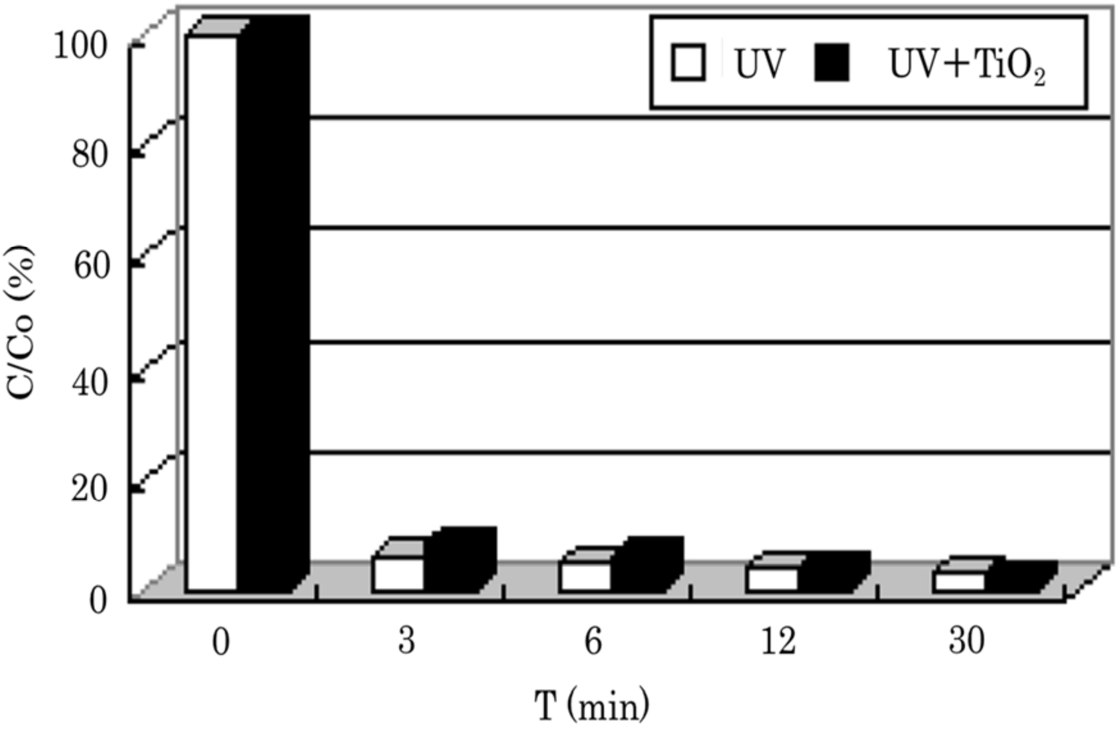


Figure 2-6 Photodecomposition of chlorthalonil

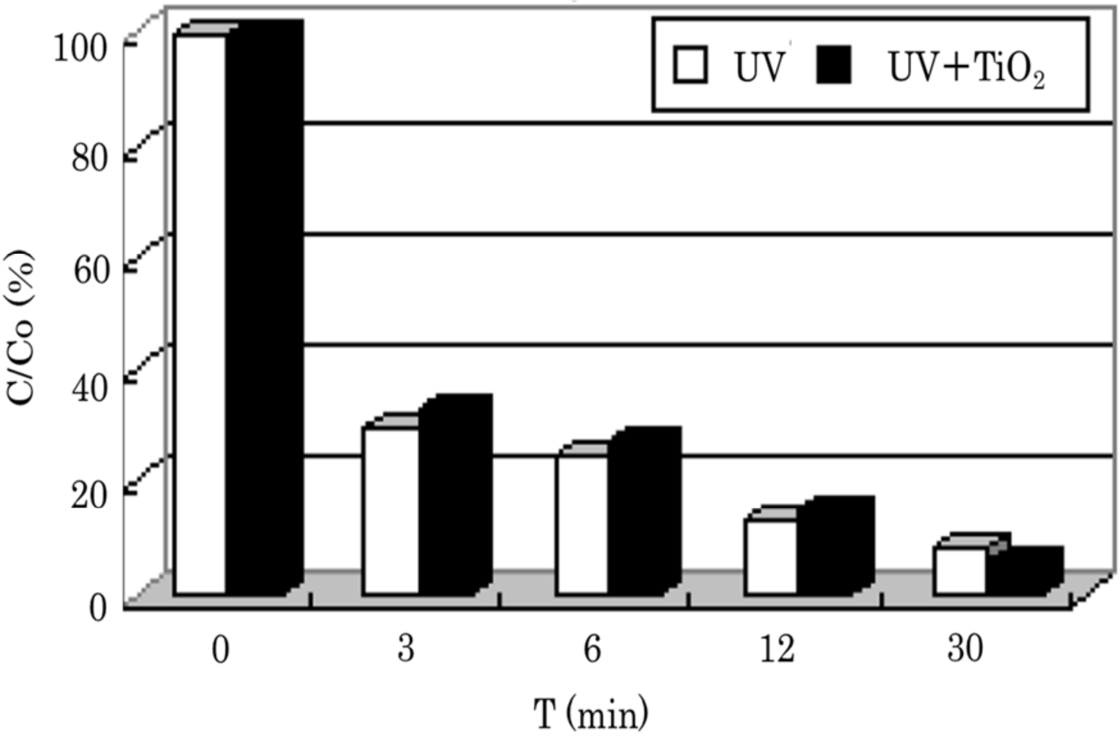


Figure 2-7 Photodecomposition of pencycuron

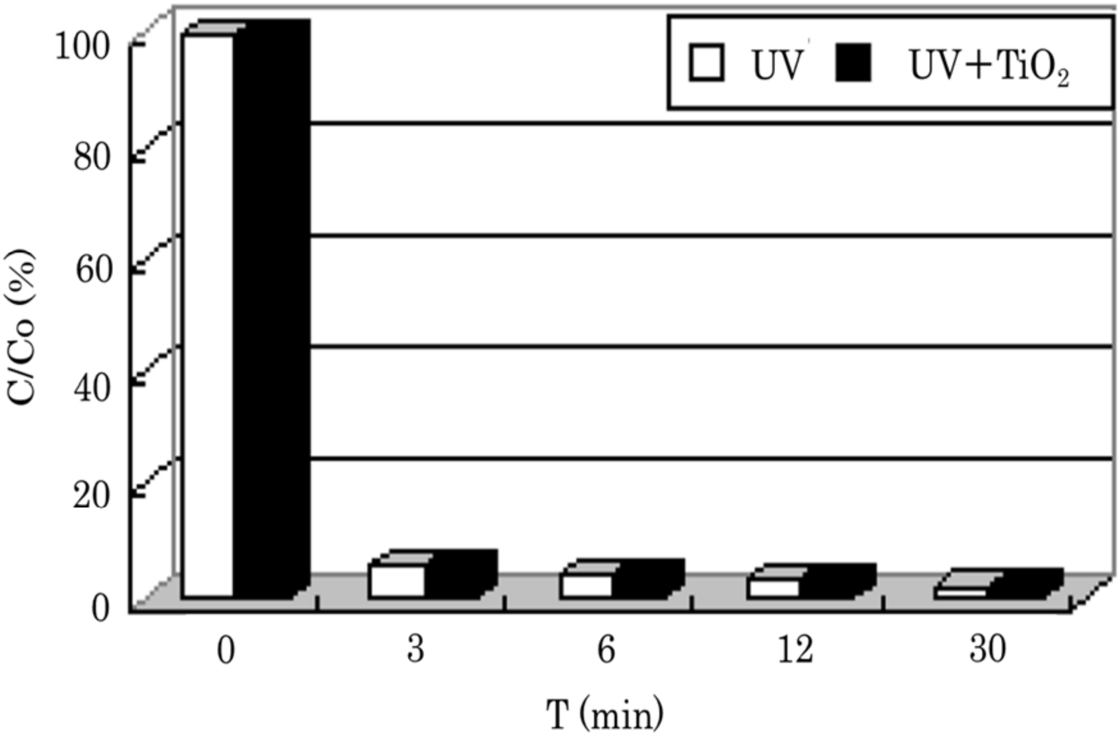


Figure 2-8 Photodecomposition of cafenstrole

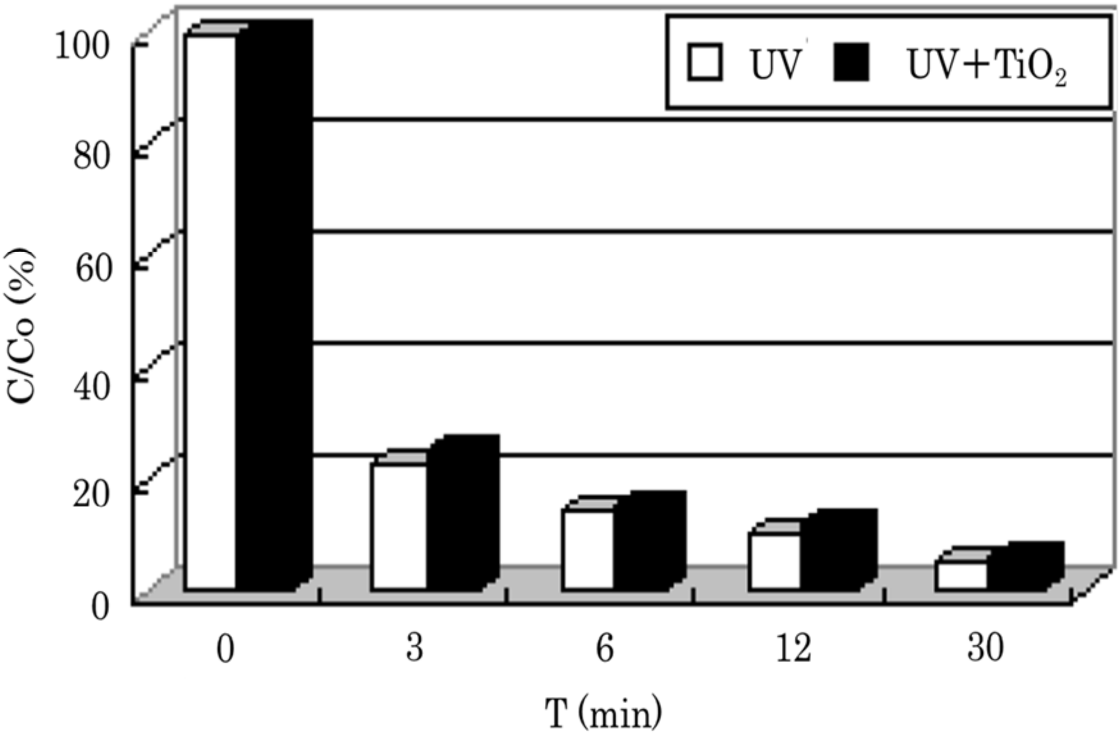


Figure 2-9 Photodecomposition of thiobencarb

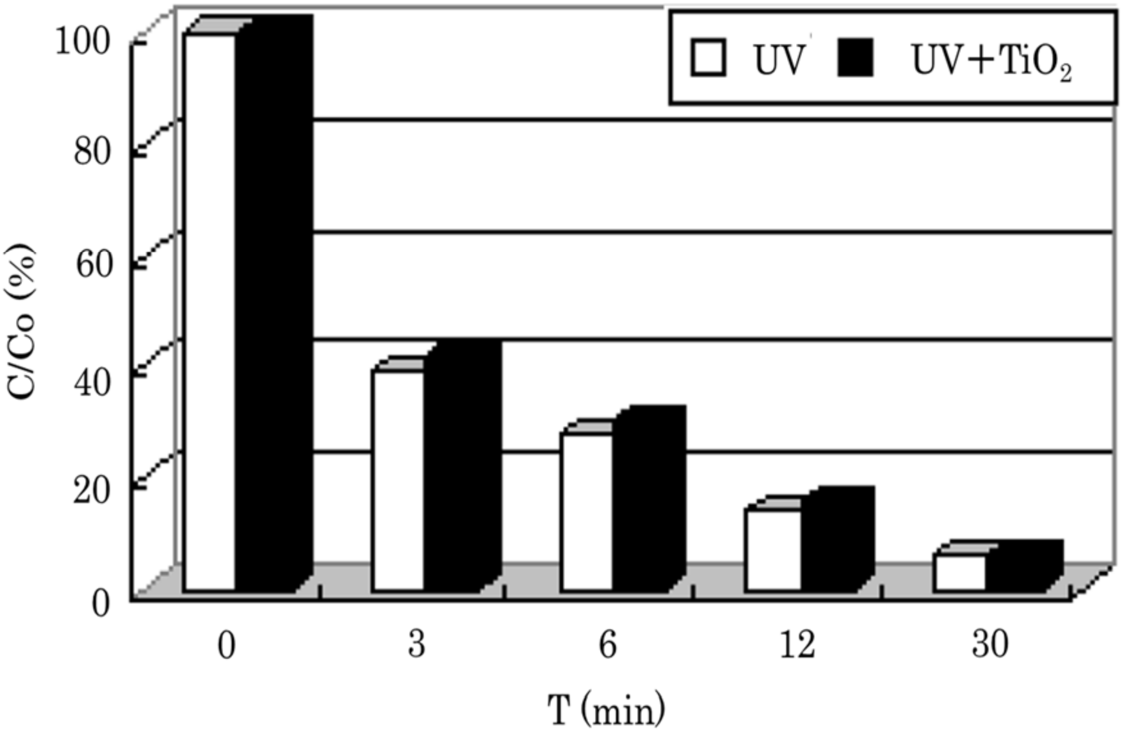


Figure 2-10 Photodecomposition of trifluralin

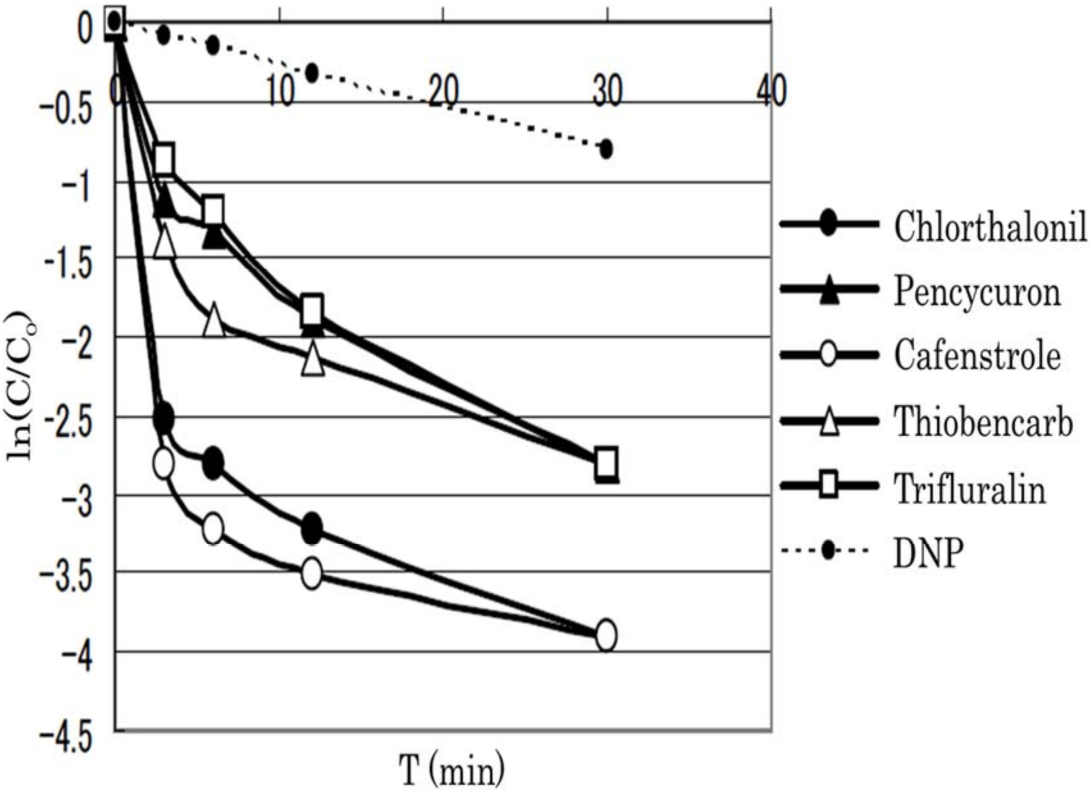


Figure 2-11 Relationship between $\ln(C/C_o)$ and the photocatalyst

Figure 2-11 shows the relationship between ln(C/C_o) and t. As these pesticides were decomposed immediately, the linear relationship between ln(C/C_o) and t could not be obtained.

Every pesticide has a biologically or chemically changeable structure in molecule. For example, a N-CO-N bond (Pencycuron and Cafenstrole) and a N-CO-S bond (Thiobencarb) are easily hydrolyzed. Cyano group (Chlorthalonil) is easily oxidized. Carbon-Cl bond, benzene ring and alkyl group are biologically hydroxylized. On the other hand, the scissions of a C-Cl bond, a C-F bond, a C-NO_2 bond, a C-NR_2 bond and an N-N bond, especially a C-Cl bond and a N-N bond, are easily occurred photochemically. Moreover, the photochemical scission of a C-Cl bond is faster than the photohydrolyses of organic phosphate esters. The differences of the photodecomposition rates in these parts would have caused the differences of the photodecomposition rate or the removal efficiency after 30 min UV irradiation of each pesticide. As the photodecomposition products could not be detected by the GC/MS analysis, it was considered that these pesticides converted into the high polar compounds.

Chapter Three - Novel Technology of Hydroxyl Radical Generation Comprehensively Using Ozone, Ultraviolet Illuminating, Ultrasonic and Titania Nanotube Photocatalyst

3.1 Introduction

Ozone is a strong oxidant and disinfectant that is commercially used for water treatment and sterilization. However, the direct reaction of ozone is quite selective in actual practice, because ozone has a very low reactivity toward aromatics substituted with electron-withdrawing groups (-COOH, -NO2) and compounds with single bond. And residence time of ozone is long, so often causing poisoning. Now, the hydroxyl radical is intensely concerned. The hydroxyl radical is often referred to as the "detergent" of the troposphere and it plays a central role in the oxidation and removal of many atmospheric compounds, because it reacts with many pollutants, often acting as the first step to their removal. The most powerful advanced oxidation systems are based on the generation of hydroxyl radicals. The hydroxyl radical is an extremely powerful oxidation agent, second only to fluorine in power. The hydroxyl radical is conventionally produced by the reaction of dissolved ozone. Hydrogen peroxide or ultraviolet light is used for decomposition of the dissolved ozone. However, the radical production efficiency of the conventional method is not high, as one hydroxyl radical is produced from three molecules of ozone. For this reason, a high-efficiency hydroxyl radical production technique for wastewater and soil treatment is desired. In order to largely promote hydroxyl radical generating efficiency, the technology is developed which comprehensively uses ozone, ultraviolet illuminating, ultrasonic and titania nanotube photocatalyst, meanwhile adopts the method of high velocity impact of forging thermal spraying. In this chapter, we can find how to improve the efficiency of hydroxyl radical generation using ozone, ultraviolet illuminating, ultrasonic and titania nanotube photocatalyst. We will explain the hydroxyl radical generation environment, and then, make optimization at last.

3.2 The formation of hydroxyl radical by ultraviolet irradiation

Ozone is a naturally occurring triatomic form of oxygen (O_3) and exists in the gas form in nature. Familiar sources of ozone are lightning in the atmosphere, the sun's UV in the upper stratosphere creating the infamous "ozone layer", and copy machines or laser printers. Ozone forms when oxygen comes in contact with ultraviolet energy wavelength of 185 nm (Eq. 1). The UV energy splits the oxygen molecule which then reattaches to another oxygen molecule:

$$3O_2 + \mathrm{UV185nm} \rightarrow O + O + 2O_2 \rightarrow 2O_3 \qquad (1)$$

The resulting unstable ozone gas molecule wants to revert back to the stable diatomic oxygen molecule (O_2). In order to do this, it must react with another compound or transfer energy through another source. This makes ozone an oxidizer. In fact, it is one of the strongest oxidizers known to man. Dissolving this gas into water makes for a very potent antimicrobial solution, which can then be used as a sanitizing agent. Ozone is different than most sanitizers because it is a gas and remains a gas during the sanitization process. It does not return into an ionic form like chlorine and therefore is much harder to stabilize in water.

The O_3/UV process makes use of UV photons to activate ozone molecules, thereby facilitating the formation of hydroxyl radicals. Because the maximum absorption of ozone molecules is at 253.7 nm (Eq. 2) (Eq. 3), the light source commonly used is a low-pressure mercury lamp wrapped in a quartz sleeve. The Low-pressure mercury lamp is shown as figure 2-7. It can generate the UV light at a wavelength of 200~280 nm. The reaction mechanism starts with activating the ozone molecule by UV to form oxygen radicals, which then combine with water to form hydroxyl radical (Eq. 4):

$$O_3 + \mathrm{UV254nm} \rightarrow O_2 + O(1D) \qquad (2)$$

$$O(1D) + H_2O \rightarrow 2\cdot OH \qquad (3)$$

Meanwhile, Later, Peyton and Glaze (1988) observed that the UV photolysis of ozone would also yield H_2O_2:

$$O(1D) + H_2O \rightarrow H_2O_2 \qquad (4)$$

In addition to that formed by

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \qquad (5)$$

The formed H_2O_2 could be further photolyzed to form two hydroxyl radicals (Eq. 5). Alternatively, it could be first dissociated into HO_2^- and then participate in a series of chain reactions along with ozone to produce hydroxyl radical as occurs in the O_3/H_2O_2 process. As the photolysis of H_2O_2 molecules is very slow, the second pathway is most likely to be predominant at neutral pH range for ozone decomposition. Thus, the O_3/UV process resembles the O_3/H_2O_2 process in terms of reaction mechanisms, and the increased rate of organic destruction can be explained by H_2O_2 catalyzed decomposition of ozone.

Weissler investigated the effect of volatile scavengers, acrylamide, formic acid, and allylthiourea on the sonochemical yield of hydrogen peroxide in oxygen and argon saturated aqueous solutions. From these experiments it was inferred that H202 is formed by the recombination of hydroxyl radicals.

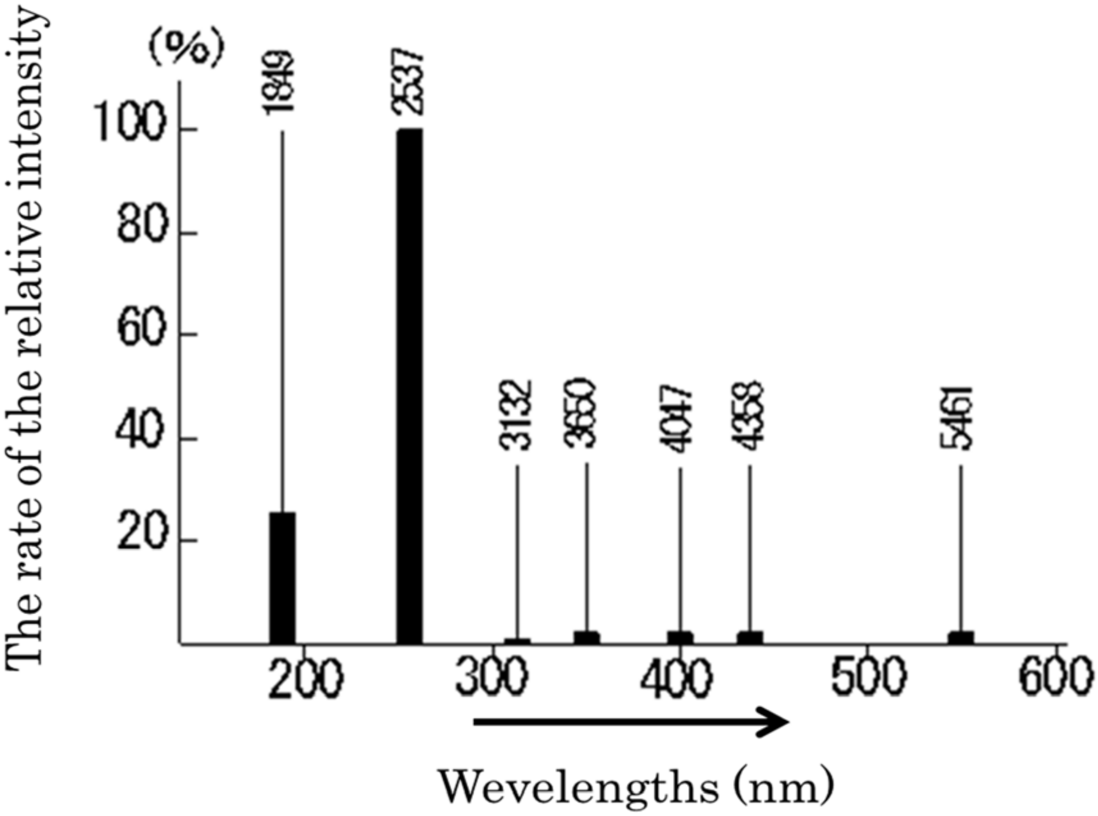


Figure 3-1 Low-pressure mercury lamps

Under UV irradiation, H_2O_2 will be photolyzed to form two hydroxyl radicals (Eq. 6). Then the formed hydroxyl radical reacts with organic contaminants or undergoes an H_2O_2 decomposition–formation cycle:

$$H_2O_2 + UV\,\lambda < 400nm \rightarrow 2\cdot OH \qquad (6)$$

$$H_2O_2 + \cdot OH \rightarrow H_2O + HO_2 \qquad (7)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (8)$$

This decomposition–formation cycle of H_2O_2 was used to explain a nearly constant concentration of H_2O_2 during treatment as observed by Benitez et al. (1996). It is interesting to note that the H_2O_2 will also act as a scavenger for hydroxyl radical as shown earlier, in which case an excessive H_2O_2 dose might hinder the radical degradation. On the other hand, sufficient H_2O_2 is necessary so that it can absorb UV to accelerate the generation of hydroxyl radicals. A trade-off between them will result in an optimum H_2O_2 dose, which still needs to be verified experimentally. Unlike ozone, H_2O_2 has an exceptionally low molar absorptivity within the wavelength range of 200~300 nm. Thus, it is particularly susceptible to the competing absorption of UV by organic compounds and suspended solids in water. If organic compounds after activation could more rapidly react with H_2O_2, such direct photo oxidation would be expected to have a major contribution to the overall degradation in the H_2O_2/UV system.

In addition, if ozone is not completely decomposed to from oxygen radicals in an excited state O(1D), it means ozone has a residue. We can generate the oxygen radicals in its electronically ground state O(3P) using 365nm ultraviolet irradiation (Eq. 9):

$$O_3 + \text{UV365nm} \rightarrow O(3P) + O_2 \qquad (9)$$

Although it O(3P) has oxidation ability, it is very weak. So it has no risk. And when there is no reaction target, they react with each other to easily form safe oxygen.

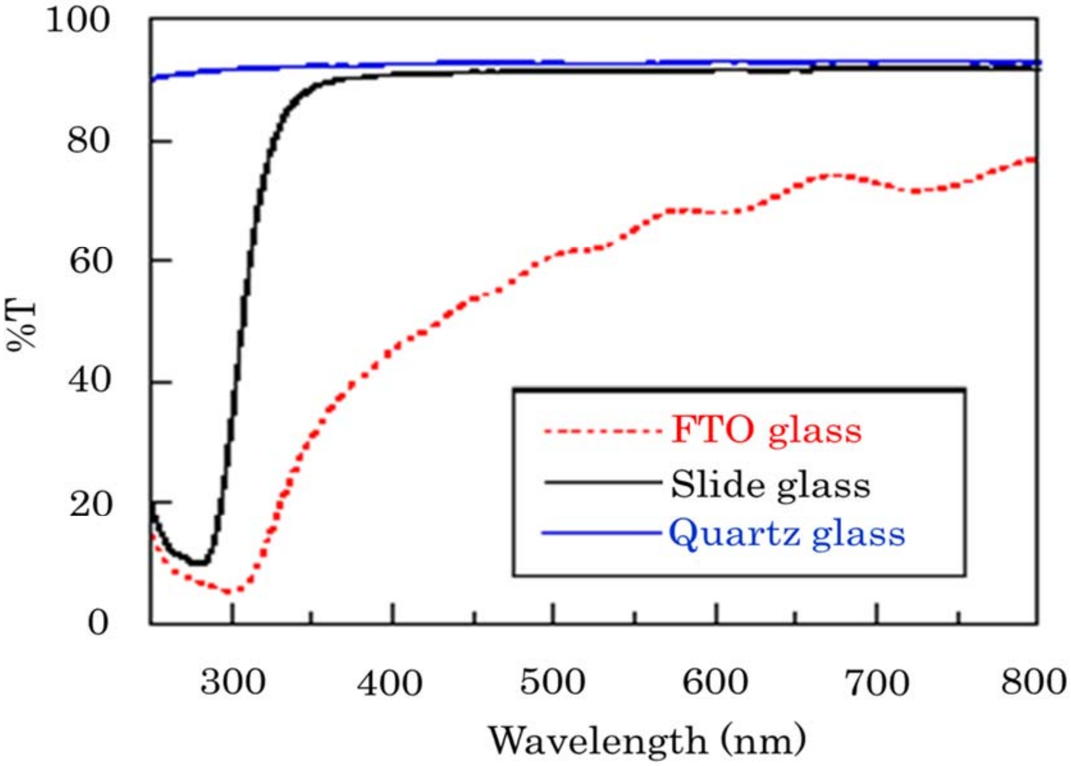


Figure 3-2 Transmission spectrum of the FTO glass, S1112 slide glass and synthetic quartz glass

From figure 3-2, we could find that synthetic quartz glass was the best result than FTO glass and slide glass in the transmission of ultraviolet rays of 385 nm or less. So, we choose the synthetic quartz glass to make the hydroxyl radical device.

3.3 Hydroxyl radical generation is assisted by TiO_2 photocatalyst

3.3.1 The formation of hydroxyl radical by TiO_2 photocatalyst

It has been believed that the TiO_2 photocatalyst generated hydroxyl radical is major active species which cause photocatalytic oxidation of water. With UV irradiation, in the dry environment, the superoxide radical anion $\cdot O_2^-$ is formed by adsorbed oxygen reacting with electrons on the surface of TiO_2 photocatalyst. The introduction of water vapor provides a large amount of water and hydroxyl groups on the TiO_2 photocatalyst surface. Oxidation of water and hydroxyl groups by TiO_2 photocatalyst produces very active hydroxyl radical, which take part in the redox reactions and improve significantly the mineralization rate of organic compounds on the TiO_2 due to its high redox potential. Photocatalytical degradation is attractive for treatment of waste streams which are too dilute for incineration and too concentrated for biological treatment or contain highly toxic organic compounds. Although a number of possible degradation pathways can be envisioned, the formation and subsequent reactions of hydroxyl radicals, being a very strong oxidizing agent, are generally accepted as predominant degradation pathways of organic substrates in oxygenated aqueous solutions. TiO_2 has been known as a semiconductor exhibiting substantial photocatalytic activity. It is non-toxic and stable in aqueous solutions and relatively inexpensive. When radiation of energy equal to or greater than the bandwidth of the semiconductor is absorbed, it is showed in figure 3-3, a photon excites an electron from the valence band to the conduction band and leaves an electronic vacancy (a hole) in the valence band (h^+). The photo-generated holes at the surface of the irradiated semiconductor can oxidize a variety of hazardous species directly to water or produce hydroxyl radical.

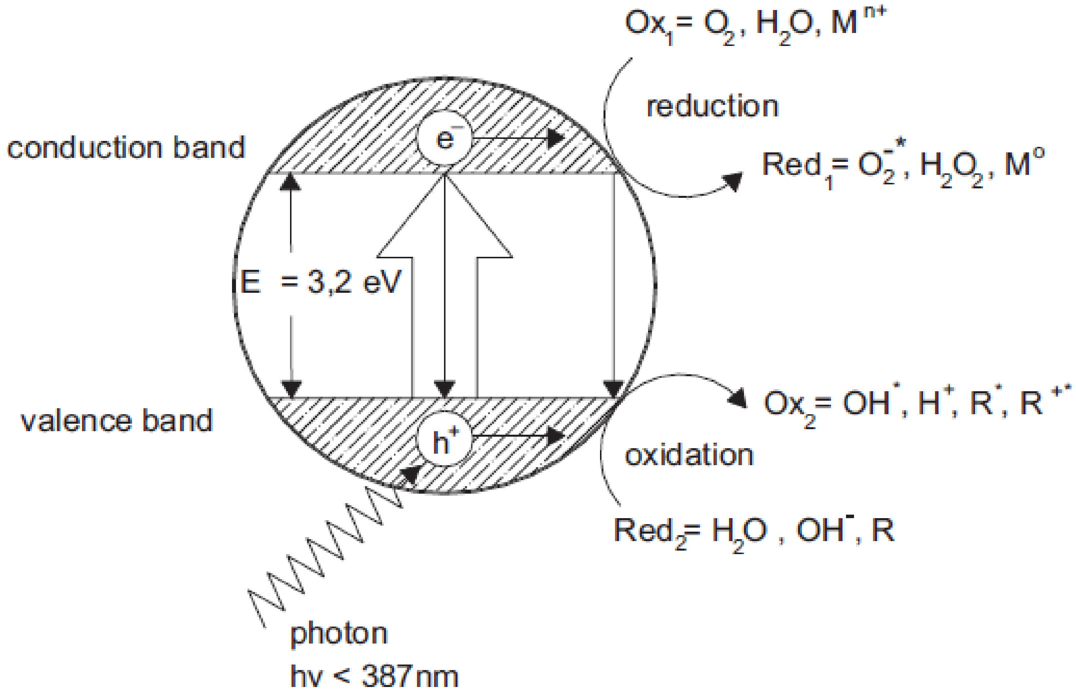


Figure 3-3 Mechanism of hydroxyl radical generation by TiO_2 photocatalyst

3.3.2 Titania nanotube loaded site-selectively with metal nanoparticles

TiO_2 is a very important material that possesses selfcleaning, anti-fogging and air-cleaning functions, etc. Heterogeneous photocatalysis, using TiO_2 as the photocatalyst, is a useful technique for the degradation of many contaminants in air, in water or on solid surfaces. Photocatalytic reactions take place when the semiconductor particle absorbs a photon of light which is more energetic than its bandgap. Thus an electron is excited from the valence band to the conduction band, leaving a hole at the valence band. In aqueous solutions the hole may be trapped by H_2O or OH^- adsorbed at the surface, thus forming the highly reactive hydroxyl radical, which can promote the oxidation of organic compounds. In order to generate hydroxyl radical and hydrogen radical as much as possible, we adopt titania nanotube loaded site-selectively with Pt nanoparticles in the device, which is characterized by the detachment of oxidization field and reduction field. Previously, TiO_2 photo-catalyst, as an active application product, has an obvious drawback when developing, that for spherical TiO_2 nanoparticles, oxidization status and reduction status can coexist on the same particle surface. This will result in a large decrease in the photoreaction function of photocatalyst because coexistence of oxidization and reduction will easily evoke back reaction. By illustrating the reactivity point on the TiO_2 particles surface, which is not studied before, and developing the particle surface control method and crystallization composition control method, we conquered the questions mentioned above. What we now are trying to develop and apply, titania nanotube loaded site-selectively, can detach the oxidization status and reduction status at nano level with the help of the inner side and external side of the cylinder structure. Moreover, it discriminately deposits Pt nanoparticles in the inner wall of the nanotube, constructing a place where reduction reaction has the priority to react independently. Then the external wall can act as an oxidization field. At nano level, due to the detachment of the reaction fields, the occurrence of back reaction can be basically restrained, forming high photo-catalyst reactivity. The structure is showed in figure 3-4. The titanium dioxide photocatalyst with such a structure is far more sensitive to ultraviolet rays than common photocatalyst in the market.

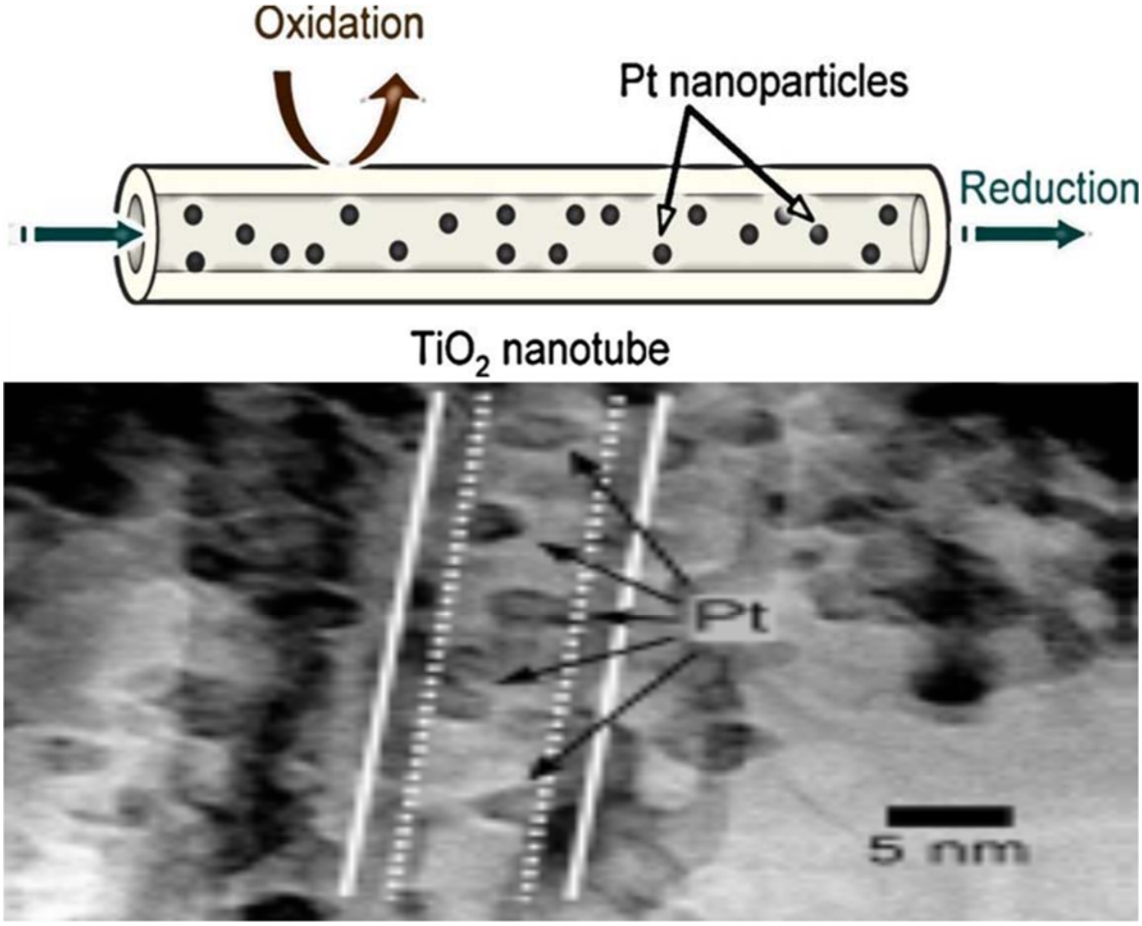


Figure 3-4 Model and TEM images of a titania nanotube (TNT) loaded site-selectively with Pt nanoparticles (from Dr. Teruhisa Ohno).

3.3.3 Development of an S-doped titania polyhedron site-selectively loaded with iron (III) oxide.

The discovery of photoelectrochemical splitting of water on titanium dioxide electrodes has leaded to many investigations of semiconductor-based photo catalysis. Titanium dioxide is one of the most promising photocatalyst, and is now used in various practical applications, but converts only a small UV band of solar light, about 2-3%, because of its large band qap of 3.2 eV. Therefore, the development of a more efficient titanium dioxide photocatalyst with a higher photocatalyst with a higher photoelectric conversion of visible light is needed. Our cooperative partner who was Professor Teruhisa Ohno from department of applied chemistry faculty of engineering, kyushu institute of technology investigated an S-doped titania nanotube (TNT) loaded with Fe_2O_3 nanoparticles in order to improve photocatalytic activity of S-doped TNT under visible light irradiation. S-doped TNT was successfully prepared using the solid-phase method at 350 °C under aerated conditions. Loading of Fe_2O_3 on S-doped TNT remarkably improved the photocatalytic activity of S-doped TNT. And it is possible that the efficiency of charge separation between photoexcited electrons and holes was improved because the electrons were trapped by Fe_2O_3. Enhancement of photocatalytic activity was strongly dependent on the site of Fe_2O_3 nanoparticles loaded on TNT, and the photoexcited electrons transferred to Fe_2O_3 from S-doped TNT under UV light irradiation or to S-doped TNT from Fe_2O_3 under visible light irradiation. They had been proven by Professor Teruhisa Ohno using PA spectra measurement, which was performed in order to elucidate the mechanism of activity improvement.

But, S-doped TNT which was loaded by Fe_2O_3 nanoparticles does not achieve the desired effect for hydroxyl radical generation. Its photocatalytic activities under UV light and visible light irradiation were not sufficient for practical applications. So, Professor Teruhisa Ohno developed relatively higher level of activity in practice in a real application, when irradiated by ultraviolet rays of less than 385 nm and visible light. The new photocatalyst structure is the crystal structure of Fe compounds on the doped TiO_2 photocatalyst. It was important in the improvement of photocatalytic activity. It was shown as figure 3-5.

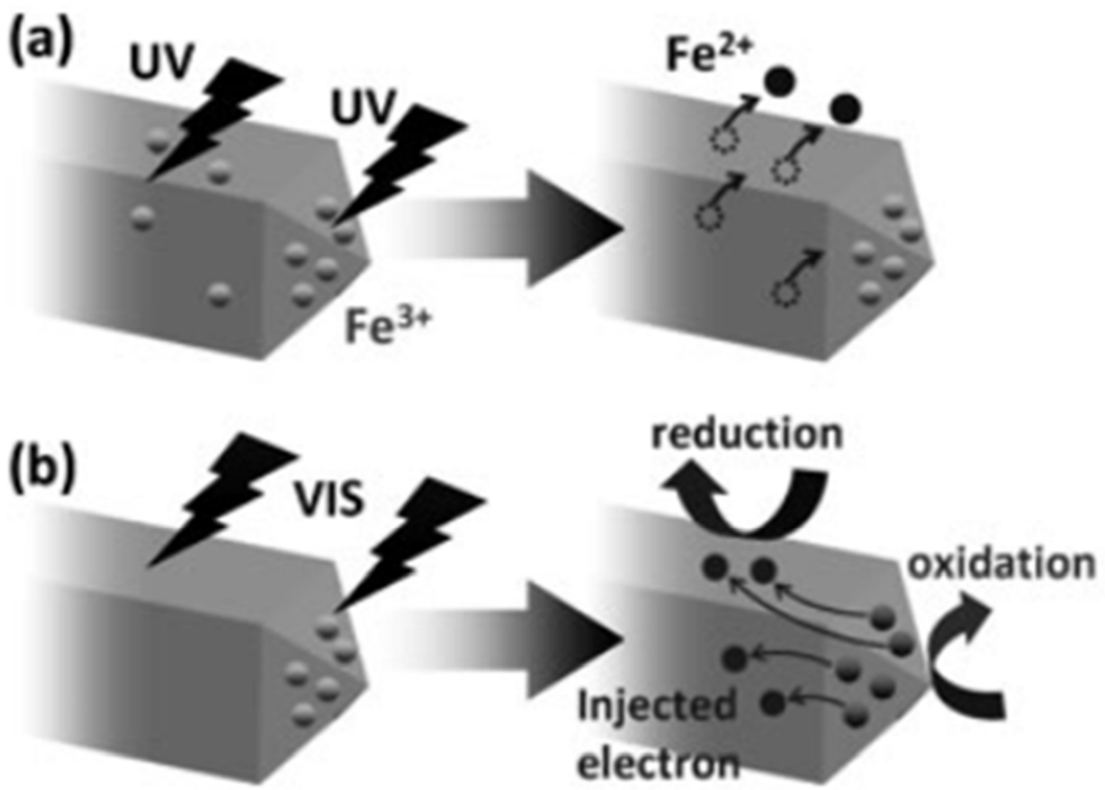


Figure 3-5 S-doped titania crystal (TC) site-selectively loaded with iron (III) oxide (from Dr. Teruhisa Ohno).

In the subsequent test, we will prove its efficiency for hydroxyl radical generation.

3.3.4 High velocity impact forging process for TiO_2 thin-film coating

TiO_2 transparent thin-film coating is an important part of the experiment device of hydroxyl radical generation. And it has a great influence on the generation of hydroxyl radical. With High Velocity Impact Forging (HVIF) thermal spraying technology, produce a layer of TiO_2 transparent thin-film coating of high density and reactivity on the surface of fused quartz. For thin-film coating, compared with traditional technology, high transparency will not influence the transmission of ultraviolet, which means ultraviolet can adequately illuminate ozone water, making it converted to hydroxyl radical; High density coating can preclude ultrasonic stripping the thin-film coating; Besides, disusing the photocatalyst organic coating dissolvent can completely expose photocatalyst to the environment, preventing most of the photocatalyst from being shaded by the dissolvent, so as to sufficiently express light reaction activity of the photocatalyst, increasing generating rate of hydroxyl radical. High Velocity Impact

Forging is a new spraying technology improved on the basis of High Velocity Oxygen Fuel (HVOF) and High Velocity Air Fuel (HVAF). When decreasing spraying temperature, it still can make the coating of spraying methods more compact, at the same time guarantee the high reactivity of photocatalyst with the low temperature. In addition, compared with the traditional film coating technology, we do not need organic solvent, when we produce a layer of TiO_2 using HVIF. It is shown as figure 3-6.

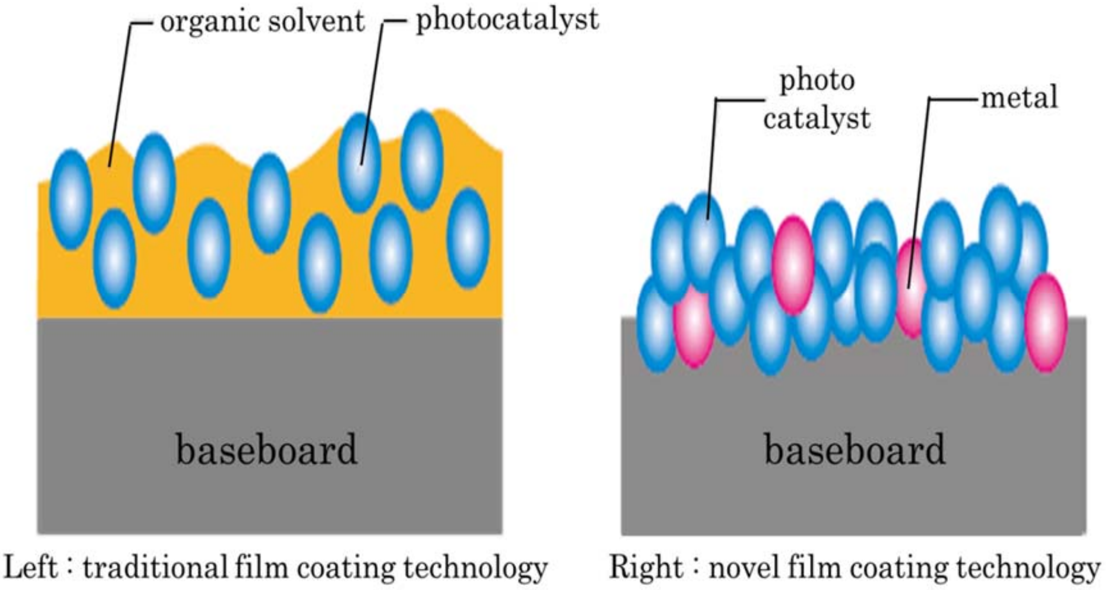


Figure 3-6 Comparison of between traditional technology and new technology on TiO_2 film coating (from Fujico Co., Ltd).

The traditional technology is to make the photocatalyst mix into the liquid that is referred to as the organic solvent. So photocatalyst is buried in organic solvent, it leads that the power and amount of photocatalyst reaction is reduced. But new technology has completely overcomes the shortcomings of the traditional technology. The photocatalytic reaction was improved significantly after the TiO_2 photocatalyst is directly and high compactly coated on the surface of the base materials by HVIF.

Of the various forms of titania (anatase, rutile and brookite) anatase is found to be the best photocatalyst. Without any chemical additives, the anatase to rutile transformation in pure synthetic titania usually occurs at a temperature range of 600-700 °C. And almost of anatase will transform into rutile at a temperature more than 800 °C. Although rutile phase has less photocatalytic activity than anatase, the mixed phase of anatase and rutile is known to exhibit enhanced photoactivity. Anatase-to-rutile phase transformation is governed by the annealing temperature, compactness of the anatase nanocrystallites. The HVIF process is a high velocity, low temperature coating process used for the production of hard facing coatings. A major advantage of HVIF processes is that we can control the temperature below 800 °C. Meanwhile, we can get a highly active and compact facing coating.

The photodecomposition and photocatalytic activities of photocatalysts were evaluated by TCD (Thermal Conductivity Detector) gas chromatograph (Shimadzu GC-8A). Figure 3-7 showed us photodecomposition effect of different photocatalyst films of Sol-gel + P25 TiO_2, HVIF + TC TiO_2, HVIF + P25 TiO_2 and blank with time change. In experiment, we measured the amount of produced carbon dioxide via oxidation of acetic acid at every 20 minutes (Eq. 10 and 11), after acetic acid was irradiated by ultraviolet. From the results, we had found HVIF + TC TiO_2 has the highest level of photocatalytic activity and efficiency of the evolution of CO_2. And we could know that TC showed photocatalytic activity under visible light irradiation longer than 254 nm, because we did different experiments that were respectively irradiated by 254nm UV and visible light irradiation. Sol-gel + P25 TiO_2 did not work efficiently and acetic acid was hardly oxidized by the Sol-gel + P25 TiO_2. But the photocatalytic activity level of HVIF + P25 TiO_2 is higher than Sol-gel + P25 TiO_2, and it was not similar to that of Sol-gel + P25 TiO_2, because we used high velocity impact forging process.

$$2CH_3CHO + 2\cdot OH + O_2 \rightarrow 2CH_3\cdot + 2CO_2 + 2H_2O \qquad (10)$$

$$CH_3COOH + h+ \rightarrow CO_2 + CH_3\cdot + H+ \qquad (11)$$

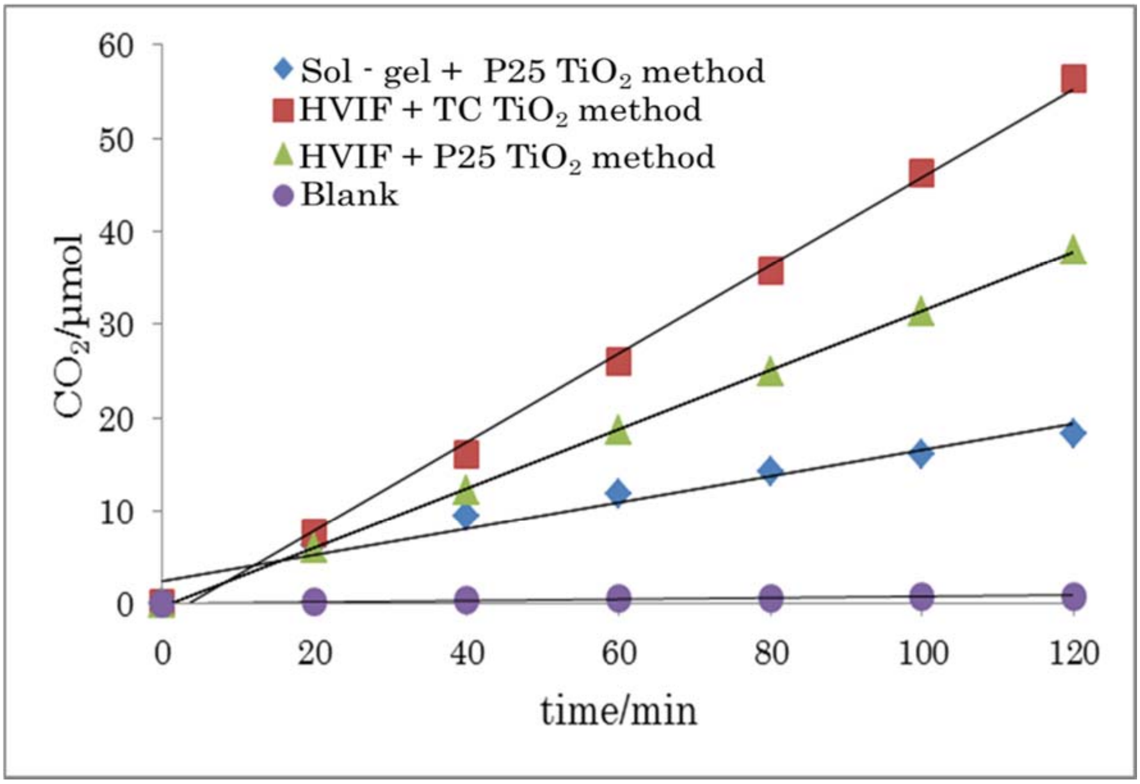


Figure 3-7 Photodecomposition effect of different photocatalyst films with time change (TC TiO_2: S-doped titania crystal site-selectively loaded with Fe_2O_3 nanoparticles)

3.4 The formation of hydroxyl radical by ultrasonic irradiation

The ultrasonic set at the bottom of the device can increase the volume of hydroxyl radical generated. The mechanism and the phenomenon of radical generation are presented in figure 3-8. Ultrasonic can produce alternating low-pressure and high-pressure waves when transmitting in solution. When the low-pressure force overpasses the intermolecular forces between solvent molecules, cavitation phenomenon occurs. The cavitation in fact is the burst after bubbles' repeated inflation and constriction. At the moment of bubbles' burst, inside the cavitation forms a limited status of high temperature, high pressure and high-speed flow. Under the conditions of high temperature and high pressure, inside the cavitation, the water molecules will be converted to hydroxyl radical and hydrogen radical through thermal decomposition. With the oxidative degradation ability of hydroxyl radical and the physical functions of ultrasonic, the polluted substances attached on the semiconductor surface can be removed. In the experiment, ultrasonic of different frequency will produce oxidant and hydroxyl radical of different concentration. By measuring the concentration of dihydroxybenzoic acid (DHBA), the product of the reaction of hydroxyl radical and salicylic acid, observe respectively the influence ultrasonic of different frequency has on the generation of oxidant. But notice that in order to decrease the damage ultrasonic impact has on semiconductor precision products, we often adopt 1~1.6 MHz ultrasonic.

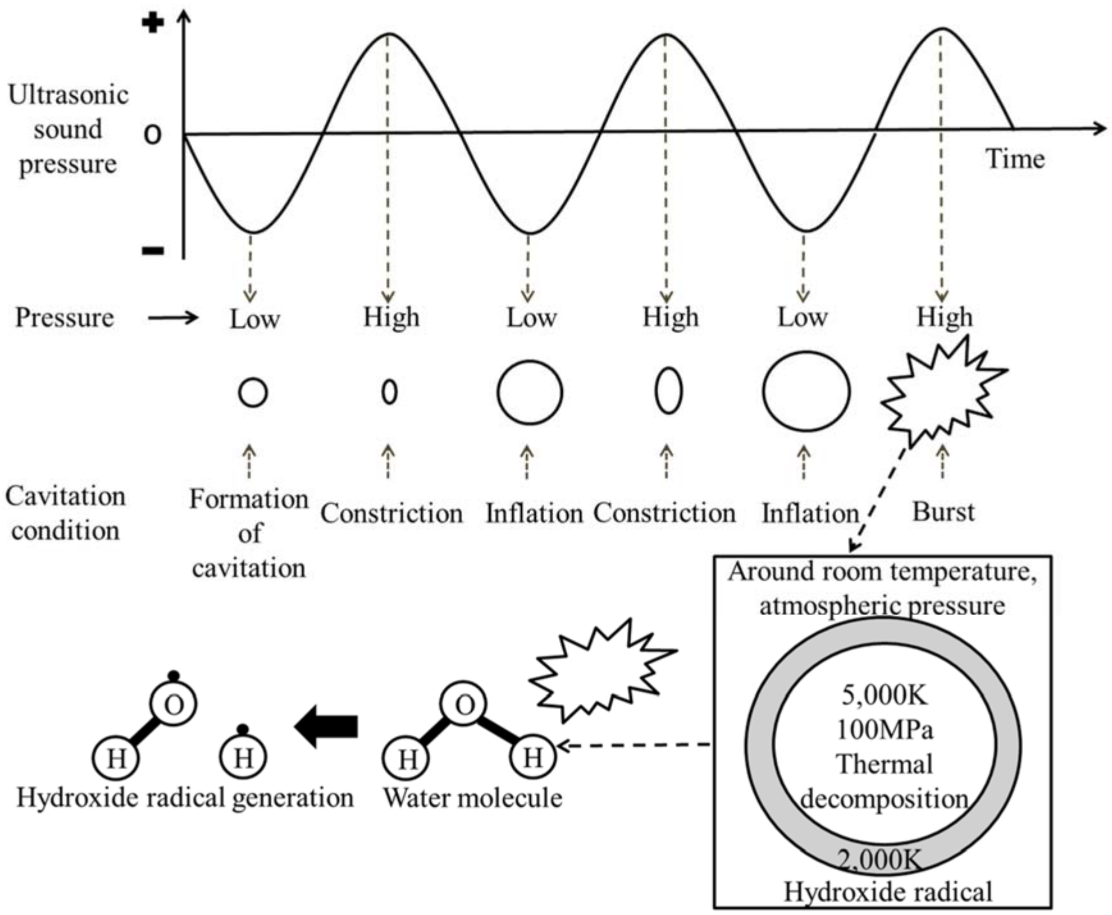


Figure 3-8 Schematic diagram is about the mechanism of hydroxyl radical generation using the ultrasonic

In addition, MHz ultrasonic could generated microbubbles and nanobubbles of having a diameter <50 µm, and have important technical applications due to their tendency to decrease in size and subsequently to collapse under water for increasing the life of hydroxyl radical. It took ~5 min for hydroxyl radical to return to its original state of water. Figure 3-9 schematically illustrates the key differences in behavior between normal macrobubbles and microbubbles. The former rapidly rise and burst at the water surface, whereas the latter are stable for longer periods of time underwater. Microbubbles gradually decrease in size due to the dissolution of interior gases by the surrounding water, and they eventually disappear. We have demonstrated that microbubbles can be useful in the formation of hydroxyl radical due to their ability to alter the nucleation condition and their efficient gaseous solubility. The relationship between the interior gas pressure and the bubble diameter is expressed by the Young–Laplace (Eq. 12):

$$P = P_l + 2\sigma / r \qquad (12)$$

Here, P is the gas pressure, Pl is the liquid pressure, σ is the surface tension, and r is the radius of the bubble. According to Henry's law, the amount of dissolved gas surrounding a shrinking bubble increases with rising gas pressure. The area surrounding a microbubble has been shown to change its state in a pressure–temperature (P–T) diagram to favor hydrate nucleation. This is a typical characteristic of microbubbles. In addition, we have found that free radicals are generated from collapsing microbubbles and it is useful in several technical applications, including the decomposition of organic chemicals and waste-water treatment. The purpose of the current study was to clarify the phenomenon of radical generation from microbubbles in the absence of dynamic stimuli, such as ultrasound or shock waves, with the aim of advancing the technical applications of this phenomenon. And we must keep that the MHz >0.8. Because if the MHz >0.8, the amount of microbubbles and nanobubbles of having a diameter <50 μm generation will drcrease.

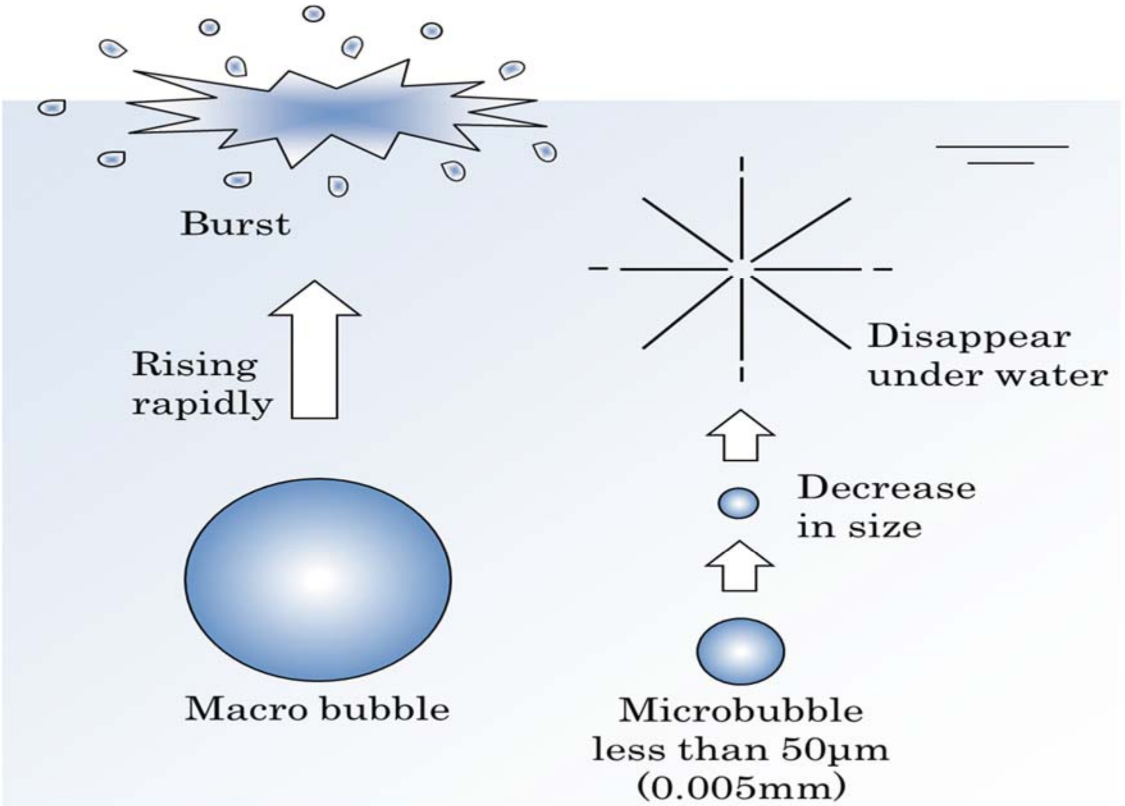


Figure 3-9 Microbubble behavior. The ordinary macrobubbles rose rapidly and burst at the surface of the water. By contrast, the microbubbles decreased in size and disappeared under the water.

3.5 Hydroxyl radical generation is assisted by Ozone

The ozone molecule consists of three oxygen atoms that are bound together (triatomic oxygen, or O_3). Unlike the form of oxygen that is a major constituent of air (diatomic oxygen, or O_2), ozone is a powerful oxidizing agent. Ozone reacts with some gases, such as nitric oxide or NO, and with some surfaces, such as dust particles, leaves, and biological membranes. These reactions can damage living cells, such as those present in the linings of the human lungs. Exposure has been associated with several adverse health effects, such as aggravation of asthma and decreased lung function. On the positive side, because of its high reactivity and its ability to harm microscopic organisms, ozone has the reputation of being an air and water purifier, only some of which it deserves. A few commercial companies market air cleaners or air "fresheners" that are said to work by generating ozone. According to the National Institutes of Health, this is a potentially harmful idea. (National Institutes of Health, 2000) In order to generate enough ozone to be effective, such equipment has to produce dangerous amounts of ozone.

In the atmosphere's wonderful self-cleansing function, ozone plays a beneficial and important role. Ozone is the primary precursor of the hydroxyl radical. The hydroxyl radical is so called because it has an unpaired electron in its outermost electronic orbit. Unpaired electrons are "lonely" and readily pair up with others, forming chemical bonds. The hydroxyl radical serves as the main scavenger in the atmosphere, reacting with a variety of compounds such as hydrocarbons, hydrogen sulfide, and carbon monoxide that would otherwise accumulate and poison us. And the ozone progressively decomposes and large quantities of hydroxyl radicals are generated. In the water, when ozone is added to water, a complex chain of reactions results in the formation of radicals, such as hydroxyl radical (Eq. 13 and 14).

$$H_2O \rightarrow HO^- + H^+ \qquad (13)$$

$$O_3 + HO^- \rightarrow HO_2^- + O_2 \qquad (14)$$

Reaction between ozone and a hydroxyl ion leads to the formation of hydrogen peroxide (Eq. 15).

$$O_3 + HO_2^- \rightarrow \cdot HO_2 + \cdot O_3^- \qquad (15)$$

A second O_3 molecule reacts with the HO_2^- to produce the ozonide radical (Eq. 16).

$$\cdot O_3^- + H^+ \rightarrow \cdot HO_3 \rightarrow \cdot OH + O_2 \qquad (16)$$

Reaction between ozonide radical and a hydrogen ion leads to the formation of hydroxyl radical.

In addition, it is well known that the hydroxyl radical has a very short live and a high reactivity. So hydroxyl radical will return into water on the moment after it is generated. However, we are looking forward to prevent hydroxyl radical returning into water with something. After we analyzed the formation of hydroxyl radical, we added ozone. When water was irradiated by ultrasonic, the water will convert into the equal volumes of hydrogen radical and hydroxyl radical, the almost of hydrogen radical and hydroxyl radical cause the immediate reaction to return the water. But we think that ozone will react with generated hydrogen radical from water, and then hydroxyl radical will be left. Mechanism is shown as figure 3-10. Left hydroxyl radical could react with pollutants.

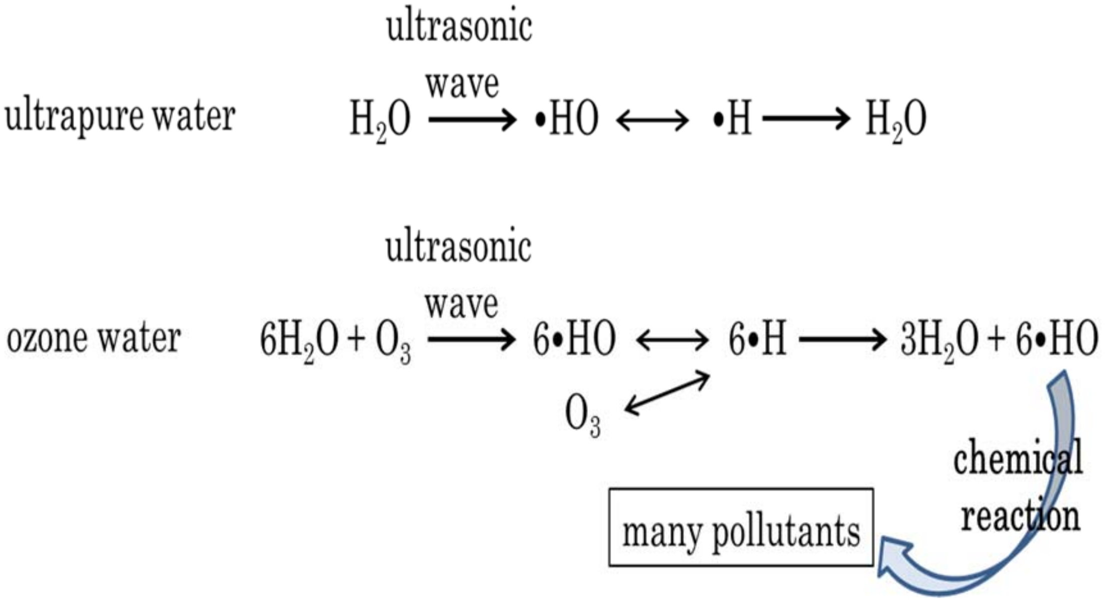


Figure 3-10 Formation of hydroxyl radical and role model

To prove the correctness of the speculation, we did an experiment. Make all kinds of gas dissolved in water, and close to saturation. They included ozone, helium, nitrogen, oxygen, argon and degas water. Then we rinsed Al_2O_3 particles on the oxidized silicon wafer surface using the MHz ultrasonic in all kinds of water. The experimental results are shown as figure 3-11.

Rinse time : 60s, MS : 1.6MHz (13.5W/cm^2)
Oxidized silicon wafer surface was polluted by Al_2O_3 particles (0.12 μm <)

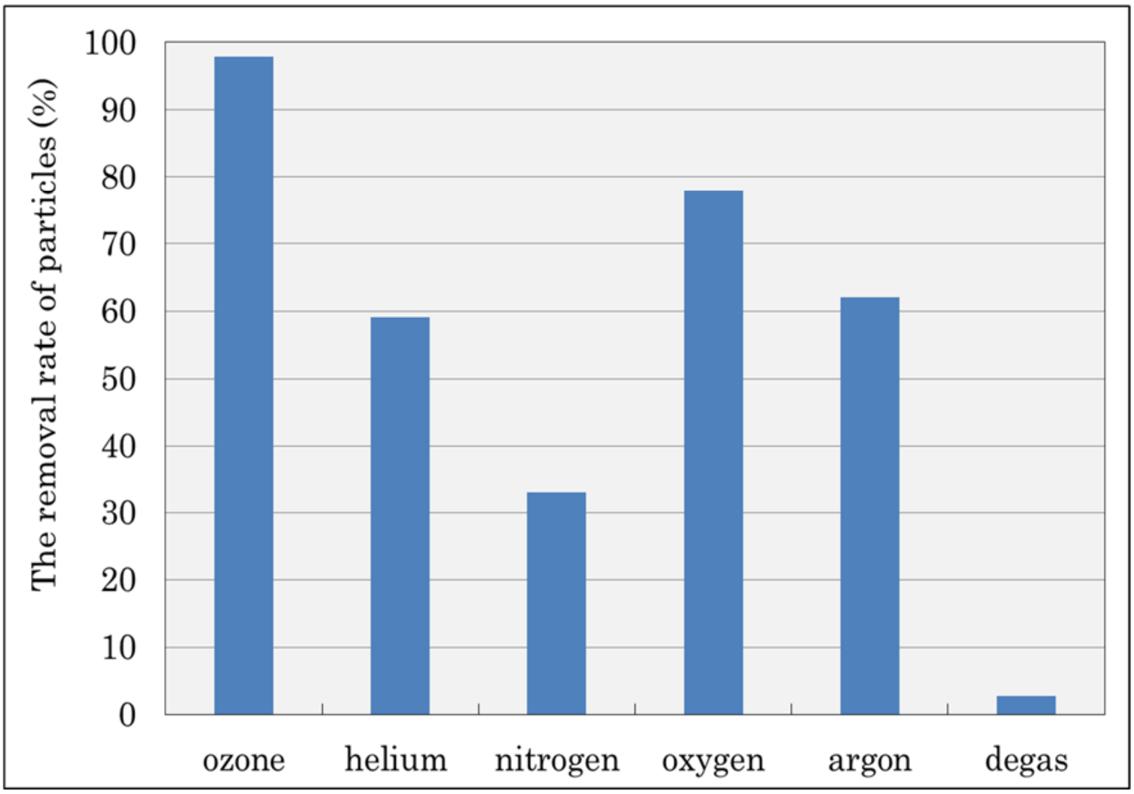


Figure 3-11 Effect of the dissolved gas to remove particles

The results show that our speculation is correct. Actually only part of the hydrogen radical can react with ozone. Because the oxidation power of hydroxyl radical is stronger than ozone, most hydrogen radical is still react with hydroxyl radical. But from figure 3-11, we can find that the cleaning effect of ozone is better than other gas, when we rinsed using MHz ultrasonic. So I think that hydroxyl radical generation is assisted by Ozone because the removal rate of Al_2O_3 particles was increased. And it is better than other gas. In addition, from the results, we could know than ozone and oxygen gas is especially effective for the removal of Al_2O_3 particles. Helium and argon that were not activated gas had the removal effect next to ozone and oxygen. Nitrogen which is usually easy to dissolve in water had the removal effect, but it was not as good as other gases. Degas was the worst, almost no effect.

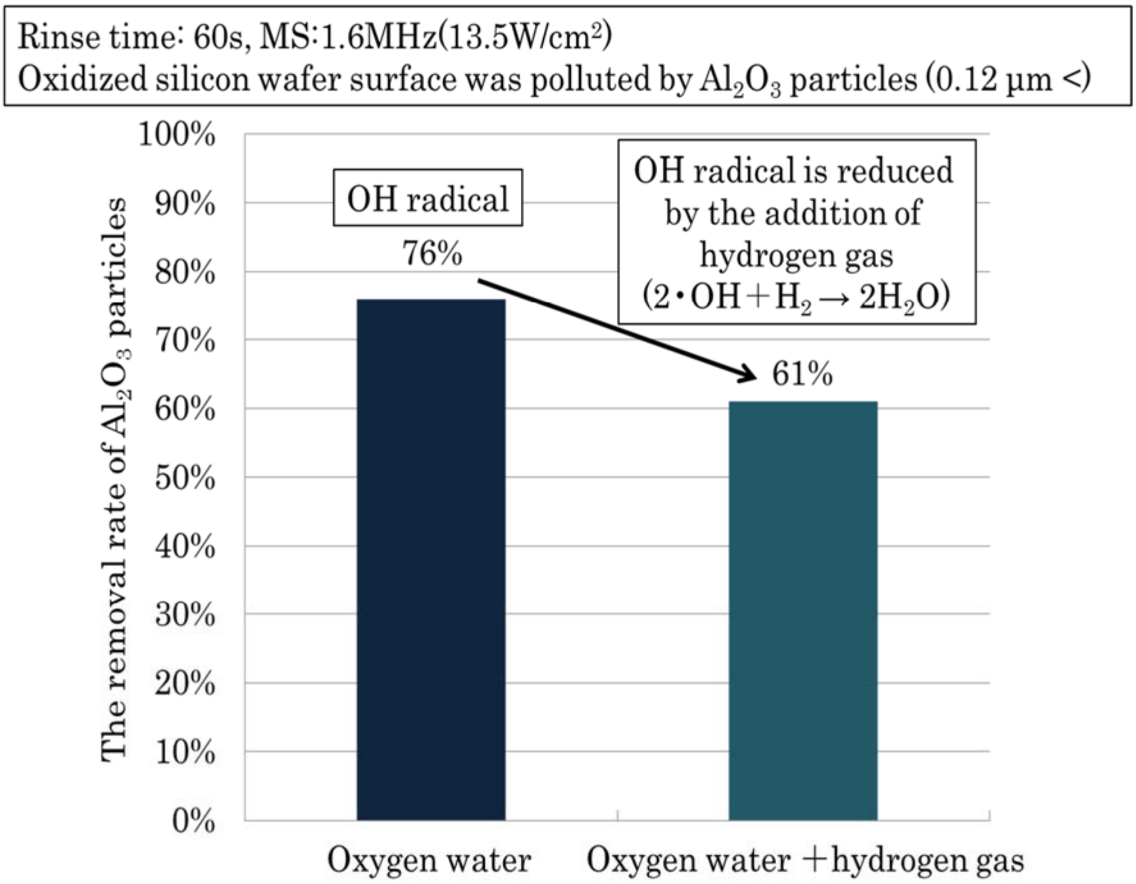


Figure 3-12 Compare oxygen water with hydrogenation oxygen water (OH radical generation verification)

Figure 3-12 show us that oxygen water was effect to remove Al_2O_3 particles on the oxidized silicon wafer surface using the MHz ultrasonic, and the cleaning effective was very high. But, when the hydrogen gas was added into oxygen water, the metal alumina particulate removal rate reduced using the MHz ultrasonic. It was inferior to the case of oxygen water alone. Meanwhile, the date can be interpreted as a phenomenon to hydroxyl radical generated by oxygen or ozone water which was subjected to ultrasonic irradiation. And hydroxyl radical was highly reactive. So it could better to remove Al_2O_3 particles

3.6 Conclusions

The contaminants that are attached to the instrument such as oil, metals and organic are usually cleaned by chemical liquid reagents. However, they cause water secondary pollution and need a lot of cost. Now objective of the study is that clean the contaminants by hydroxyl radical. But the hydroxyl radical is conventionally produced by the reaction of dissolved ozone. Hydrogen peroxide or ultraviolet light is used for decomposition of the dissolved ozone. However, the radical production efficiency of the conventional method is not high. For this reason, a high-efficiency hydroxyl radical production technique is desired. In response to this need, new technology of the hydroxyl radical. Radicals can be generated by ultrasound, ultraviolet irradiation, photocatalyst, ozone and so on. Meanwhile, MHz-ultrasound has effect on the life of the radicals. In this paper, we had been through a series of results to prove the validity and mechanism of them. It is shown as figure 3-13 and figure 3-14.

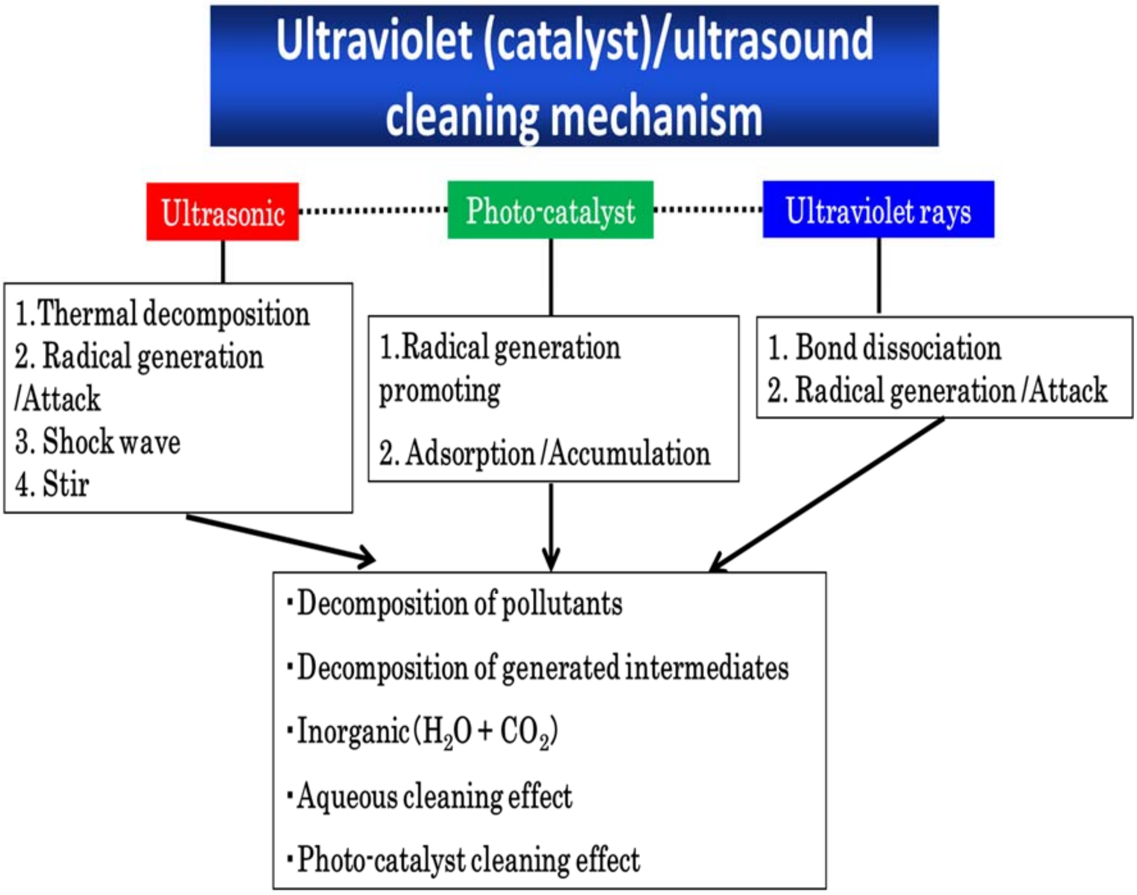


Figure 3-13 Influence factors of cleaning mechanism by hydroxyl radical

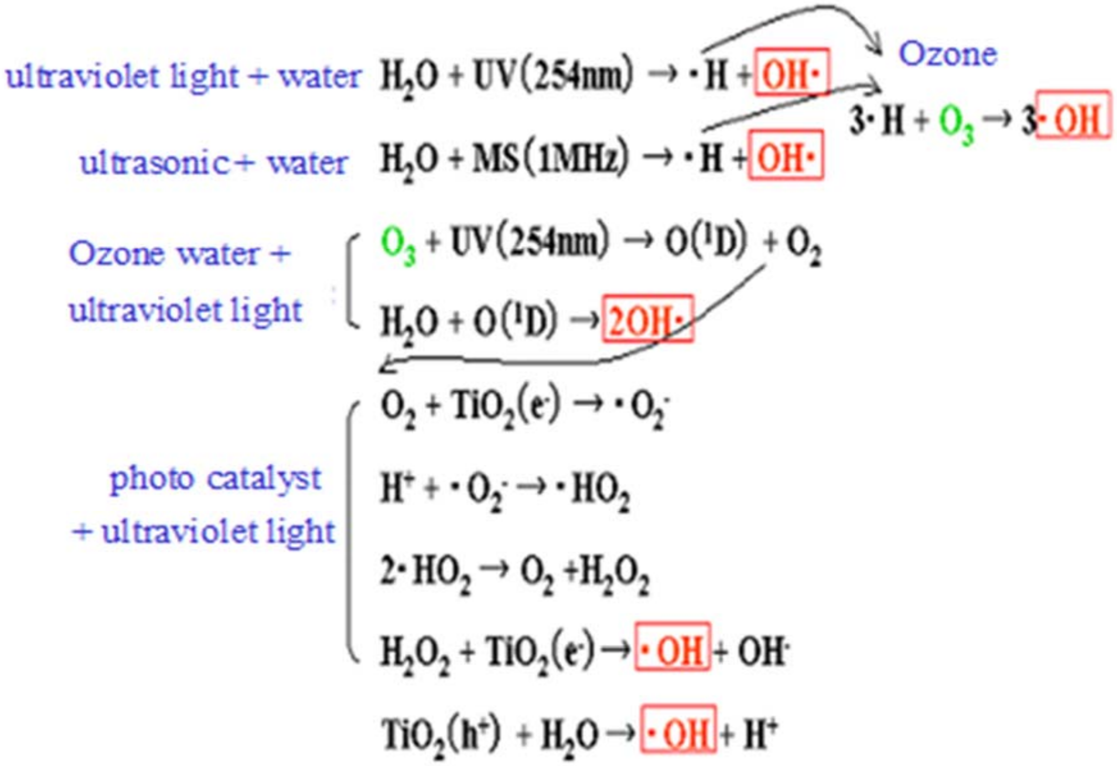


Figure 3-14 Theory of hydroxyl radical generation (UV: ultraviolet, MS: MHz ultrasonic)

Most notably hydroxyl radicals are produced from the decomposition of hydro-peroxides (ROOH) or, the reaction of excited atomic oxygen with water in atmospheric chemistry. Now our objective of this study is the development and technical analysis of washing device of hydroxyl radical water generated by 'O3-water/ultraviolet/MHz ultrasonic/TiO_2 (titanium dioxide photo-catalyst)' and we expect this method can be used for cleaning semiconductor device as environment-friendly as we can.

Chapter Four - Photo-decomposition of volatile organic compound using nano-reaction field separation TiO_2 photocatalyst

4.1 Introduction

Environmental pollution caused by chemical substances such as dioxins, polychlorinated biphenyls, pesticides, medicines, and plastic additives is a widespread issue. In addition, organic halogen compounds generated by chlorination for water purification have become a serious problem. Many chemical substances that may be found in drinking water are regulated.

Activated carbon treatment often is used to remove chemical substances that cannot be removed by other treatments. However, activated carbon treatment is relatively expensive and the spent activated carbon requires safe disposal. Recently, photo-decomposition of organic compounds with a TiO_2 photocatalyst has been reported. However, few TiO_2 photocatalysts are effective for the decomposition of chemical substances in water.

A nano-reaction field separation TiO_2 photocatalyst, for which oxidation and reduction are separated, was investigated. The photocatalyst was coated on the surface of a carrier using a low-temperature spraying method. The photocatalyst possessed a strong ability to decompose compounds and could withstand strong physical forces. The photo-decomposition of volatile organic compounds (VOCs) generated by chlorination in water purification was investigated using this TiO_2 photocatalyst.

4.2 Materials and methods

4.2.1 Reagents

Solutions of VOCs which is shown as table 4-1 were prepared by the dilution of 1,000 mg/L CH_3OH solutions obtained from Wako Pure Chemical Industries.

p-Bromofluorobenzene (internal standard) and CH_3OH for dioxin analysis were obtained from Wako Pure Chemical Industries and Kanto Kagaku, respectively. Ultra-pure water was prepared using a Japan Millipore Milli-Q SP unit.

Table 4-1 VOCs and GC/MS quantity conditions

No.	VOCs	Retention time (min)	Quantity ion
1	1,1-Dichloroethylene	7.00	61
2	Dichloromethane	8.12	84
3	*tert*-Butyl methyl ether	8.34	73
4	*trance*-1,2-Dichloroethylene	8.53	61
5	*cis*-1,2-Dichloroethylene	11.14	61
6	Chloroform	11.34	83
7	1,1,1-Trichloroethane	12.29	97
8	Tetrachloromethane	13.02	117
9	1,2-Dichloroethane	13.21	62
10	Benzene	13.30	78
11	Trichloroethylene	14.51	130
12	1,2-Dichloropropane	15.06	63
13	Bromodichloromethane	15.42	83
14	*cis*-1,3-Dichloropropene	16.46	75
15	Toluene	17.36	92
16	*trans*-1,3-Dichloropropene	17.55	75
17	1,1,2-Trichloroethane	18.22	97
18	Tetrachloroethylene	19.06	166
19	Dibromochloromethane	19.43	129
20	*m,p*-Xylene	21.13	106
21	*o*-Xylene	22.19	106
22	Bromoform	23.26	173
23	1,4-Dichlorobenzene	26.47	146

4.2.2 TiO_2 Photocatalyst

The TiO_2 photocatalyst was a nano-reaction field separation type with doped Fe and was coated on the surface of aluminium fiber (10 cm ×10 cm ×3-5 mm) using a low-temperature spraying method. It possessed high durability like figure 4-1. The coating was done at low temperature, so the crystal structure was an anatase type, which is considered to possess strong decomposition ability against organic compounds.

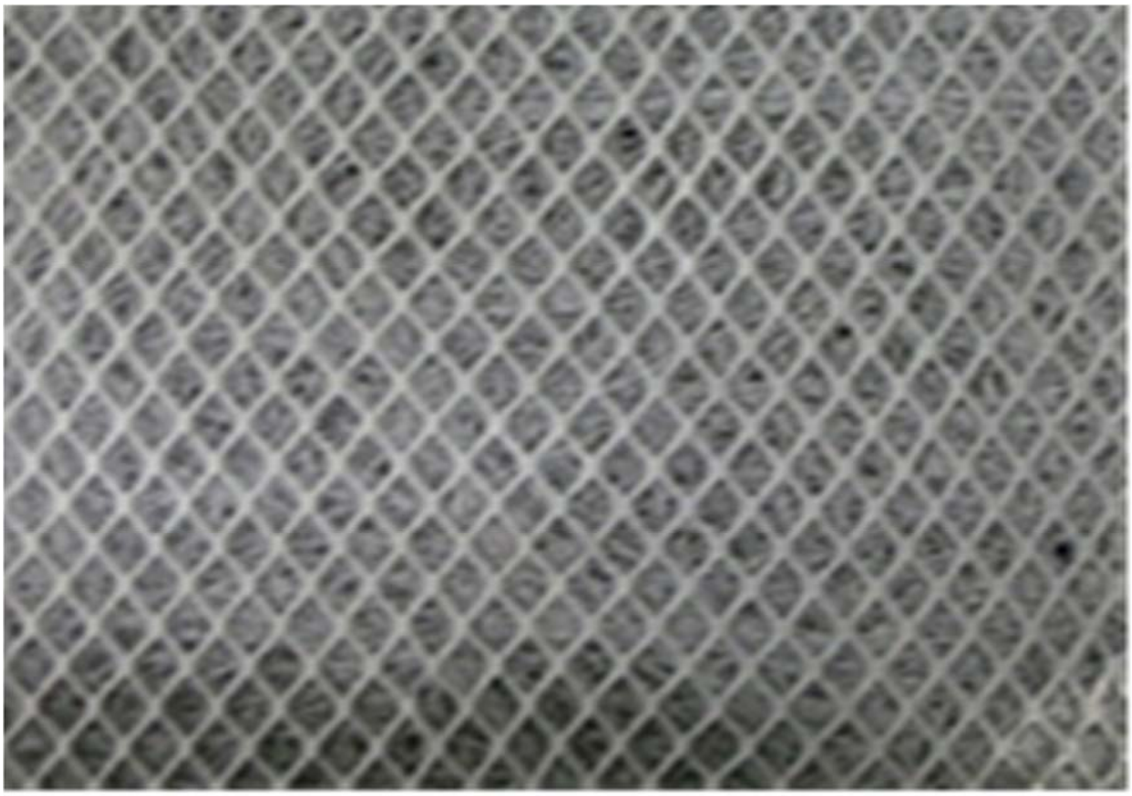
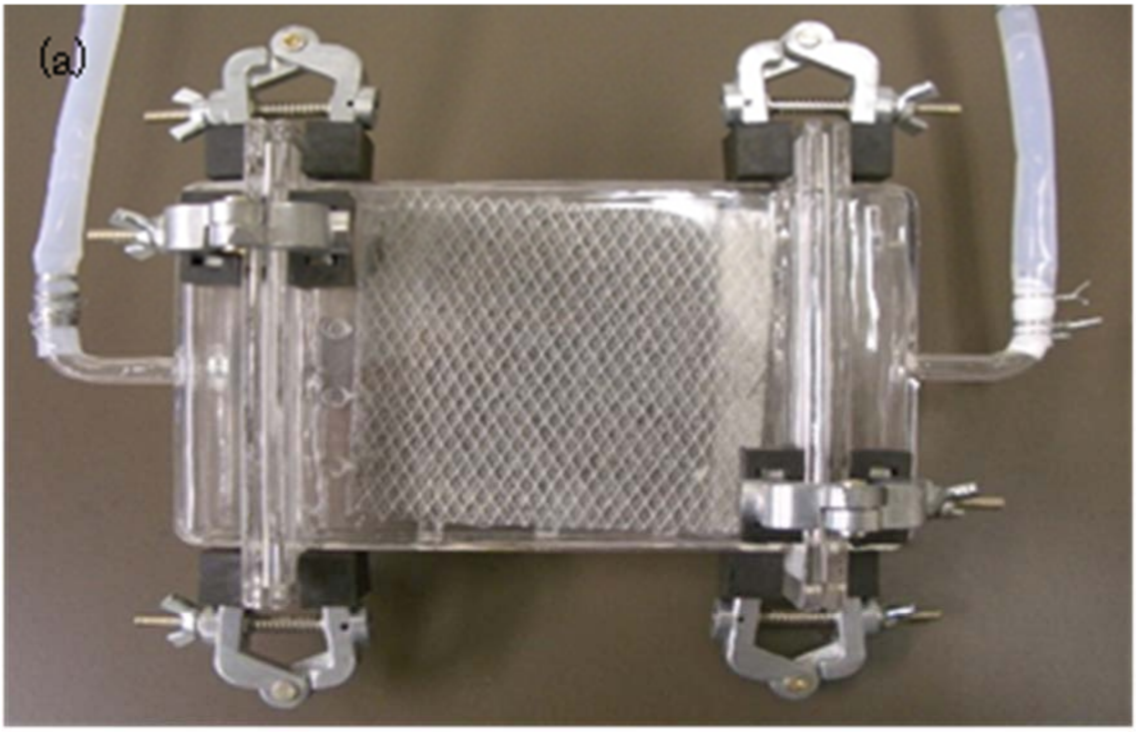


Figure 4-1 Nano-reaction field separation TiO_2 photocatalyst coated on the surface of aluminium fibber (10 cm × 10 cm × 3-5 mm).

4.2.3 Instruments

Figure 4-2a shows the reactor and photo-decomposition apparatus. The black light contained two Panasonic 6 W black lights blue FL6BL-B (main wavelength: 365 nm); the sterilizeing lamp contained a Panasonic 6 W sterilizeing lamp GL6/Q (wavelength: 254 nm) is shown as figure 4-3. The reactor was made of quartz glass (11 × 11 × 2.6 cm). The pump was a Surpass Industry Teflon bellows pump Model BP-300. Ultraviolet ray (UVR) intensity was measured on the surface of the reactor with a Topcon Technohouse UVR-2 (black light) or a Mother Tool UVC-254 (sterilizeing lamp) radiometer, respectively.



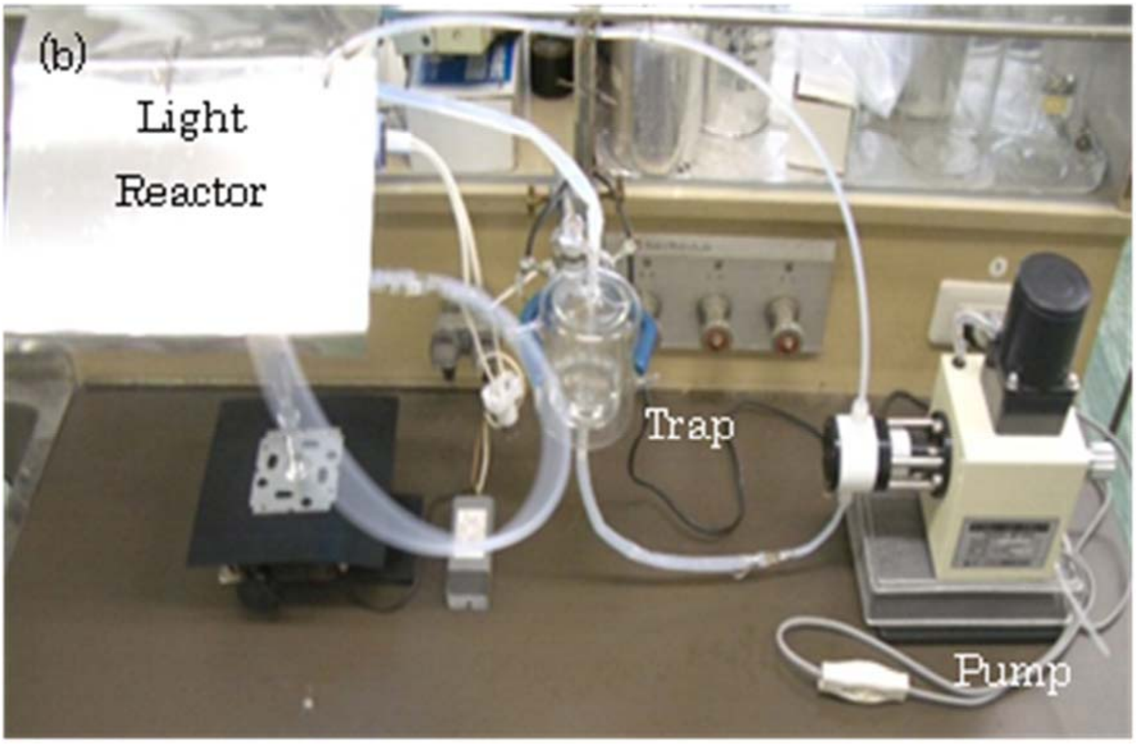


Figure 4-2 Experimental setup. (a) Reactor made of quartz glass (11 × 11 × 2.6 cm), (b) Photo-decomposition apparatus. Pump was a Teflon bellows pump.

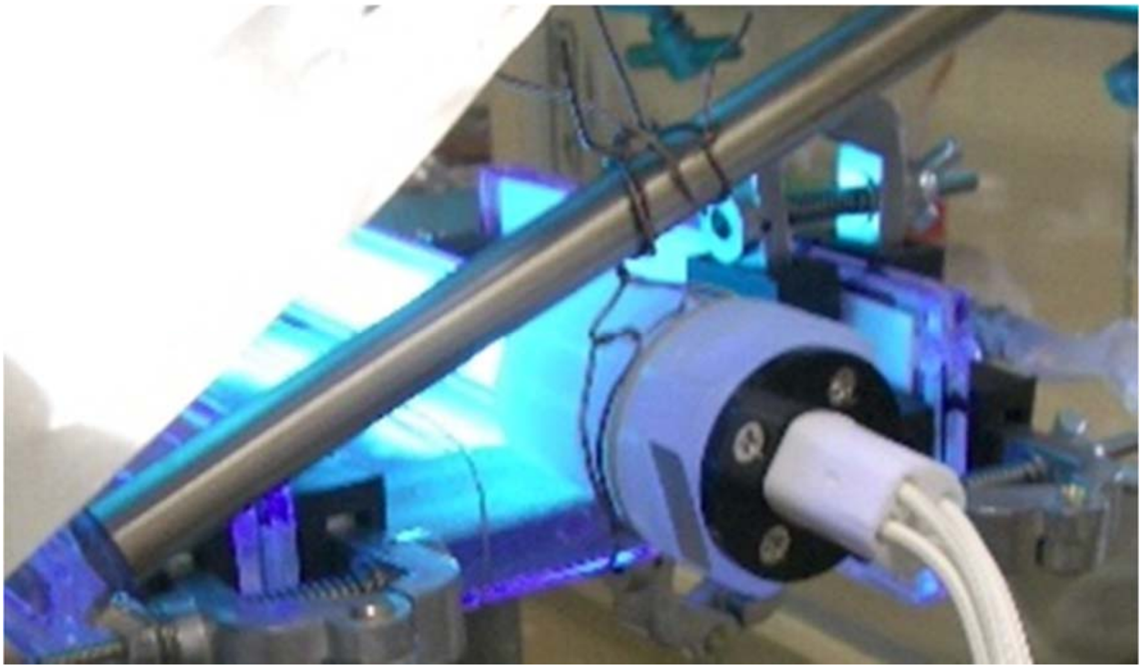


Figure 4-3 Sterilizeing lamp

The purge/trap-Gas chromatography–mass spectrometry (GC/MS) was a GL Sciences Tekmar Dohrmann aqua auto 70 liquid autosampler-4000J sample concentrator with an Agilent Technologies Agilent 6890/a Nihon Denshi JEOL Automass Sun instrument.

4.2.4 Photo-irradiation

The photocatalyst was sequentially washed with ultra-pure water, CH_3OH, and ultra-pure water. The photo-irradiation conditions are shown in table 4-2. First, the experiment was performed without irradiation and then was performed with irradiation. Samples for analysis were collected with a pipette from the trap. UVR intensity without irradiation was < 0.0002 mW cm^{-1}.

Table 4-2 Photo-irradiation conditions

Item	Black light	Sterilizeing lamp
Water temperature (°C)	25	25
Flow rate (mL/min)	200-500	500
UVR intensity (mW/cm)	2.0	3.4
Concentration (mg/L)	1	1
Volume of sample water (mL)	200-500	500

4.2.5 Analytical Methods

Ten mL sample water was placed in a 44-mL glass bottle. Ultra-pure water was added to the bottle, which was covered with a Teflon-silicone-rubber cap so that no bubbles were retained. VOCs were measured by the purge/trap-GC/MS method. The GC/MS conditions and quantities are shown in tables 4-1 and 4-3, respectively.

Table 4-3 Purge/trap-GC/MS conditions

Column	AQUATIC 0.25 mm × 60 m × 1.0 μm
Column temperature	40 °C (1 min) - 4 °C/min - 100 °C -10 °C/min - 200 °C (10 min)
Column pressure	200 kPa
Sample volume	2 μL (splitless)
Carrier gas	He
Ion source temperature	200 °C
Interface temperature	180 °C
Mode	EI (SIM)
Purge time	4.5 min
Dry purge time	3.5 min
Elution temperature	180 °C
Elution time	6 min

4.3 Results and discussion

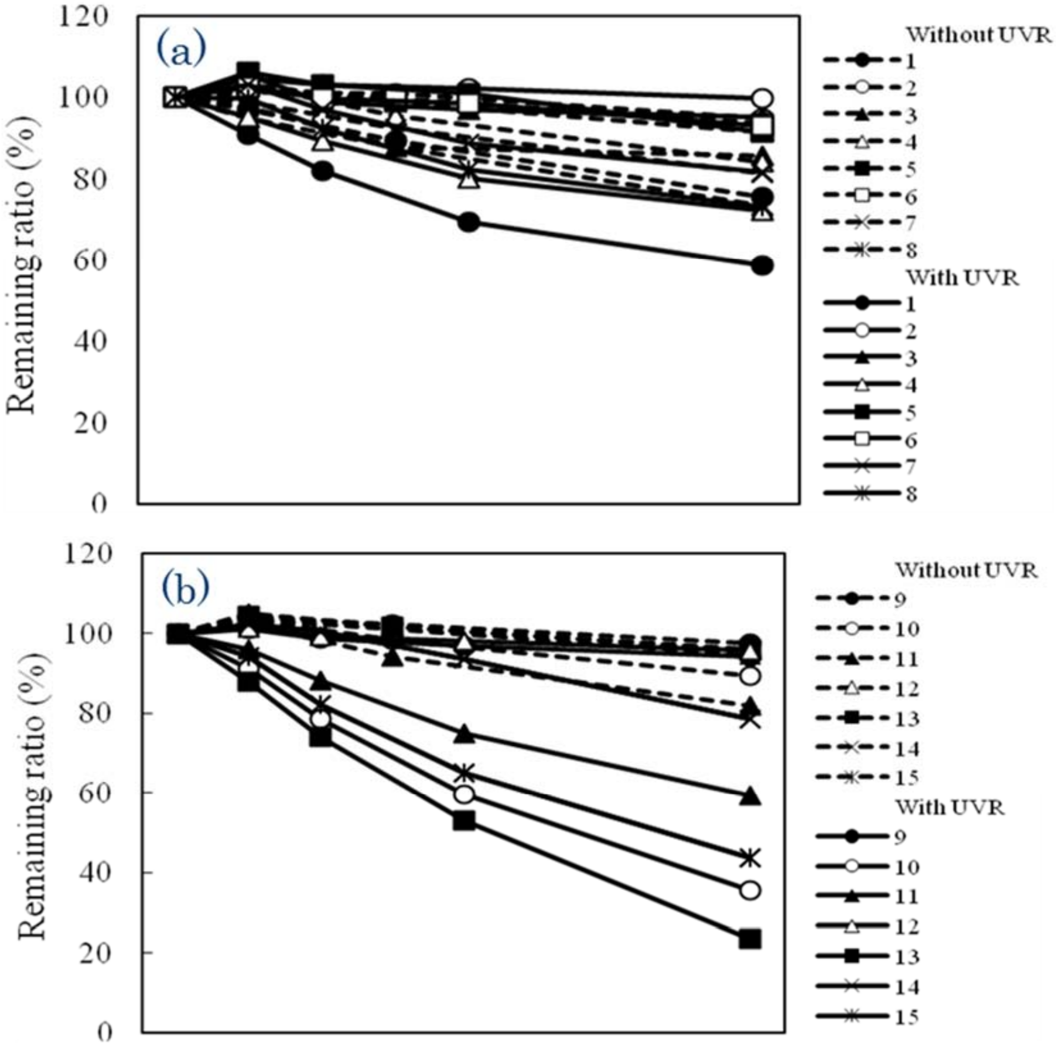
4.3.1 Black Light

At a UVR intensity of 2.0 mW cm 1 at 365 nm (0.016 mW/cm at 254 nm) and a flow rate of 200 mL/min, no difference from the blank was observed; however, at 500 mL/min, a slight difference from the blank was observed for all of the compounds except tert-butyl methyl ether, benzene, cis-1,3-dichloropropene, and tetrachloroethylene. Thus, the photocatalyst did not cause any decomposition in this wavelength range.

In general, VOCs concentrations decrease logarithmically upon adsorption and photo-decomposition. Then, the compounds decreasing linearly are considered that their volatile is contained. All tubes used were Teflon-lined to prevent the influence of the silicon tube on adsorption of compounds, which was significant.

4.3.2 Sterilizeing Lamp

A UVR intensity of 3.4 mW/cm is at 254 nm and a flow rate of 500 mL/min, a difference from the blank was observed for almost all of the compounds. More than 40% decomposition of 1,1-dichloroethylene, benzene, trichloroethylene, bromodichloromethane, toluene, tetrachloroethylene, dibromochloromethane, o,m,p-xylene, and bromoform was found after 4-h irradiation like figure 4-4b. A similar amount of decomposition of the compounds was found without the photocatalyst because of the high UVR intensity.



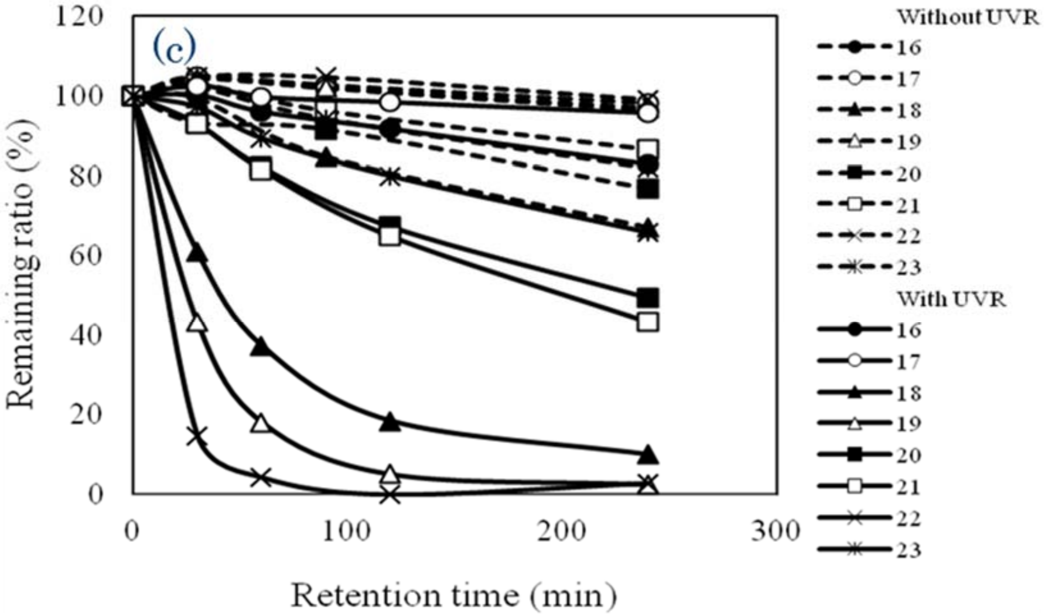


Figure 4-4 Remaining ratio of VOCs with the sterilizeing lamp. UVR intensity was 3.4 mW/cm at 254 nm and flow rate was 500 mL/min. (a) VOCs No. 1-8, (b) VOCs No. 9-15, (c) VOCs No. 16-23.

Figure 4-5a shows the relation between boiling point and amount of the compound remaining after 4-h irradiation. No obvious correlation was found for compounds with a boiling point within the range of 40-110 °C. However, a boiling point > 0 °C was considered to exert an influence. Figure 4-5b shows the relation between chemical structure and the amount of each compound remaining after 4-h irradiation. Compounds containing Cl, Br, and a double bond were easy to decompose. Compounds containing a benzene ring also were easy to decompose, unless the benzene compound contained an alkyl group or Cl. The relation between water solubility and the amount of compound remaining after 4-h irradiation was similar to correlation with dielectric constant but neither correlation was large. The results are shown as figure 4-5c and figure 4-5d.

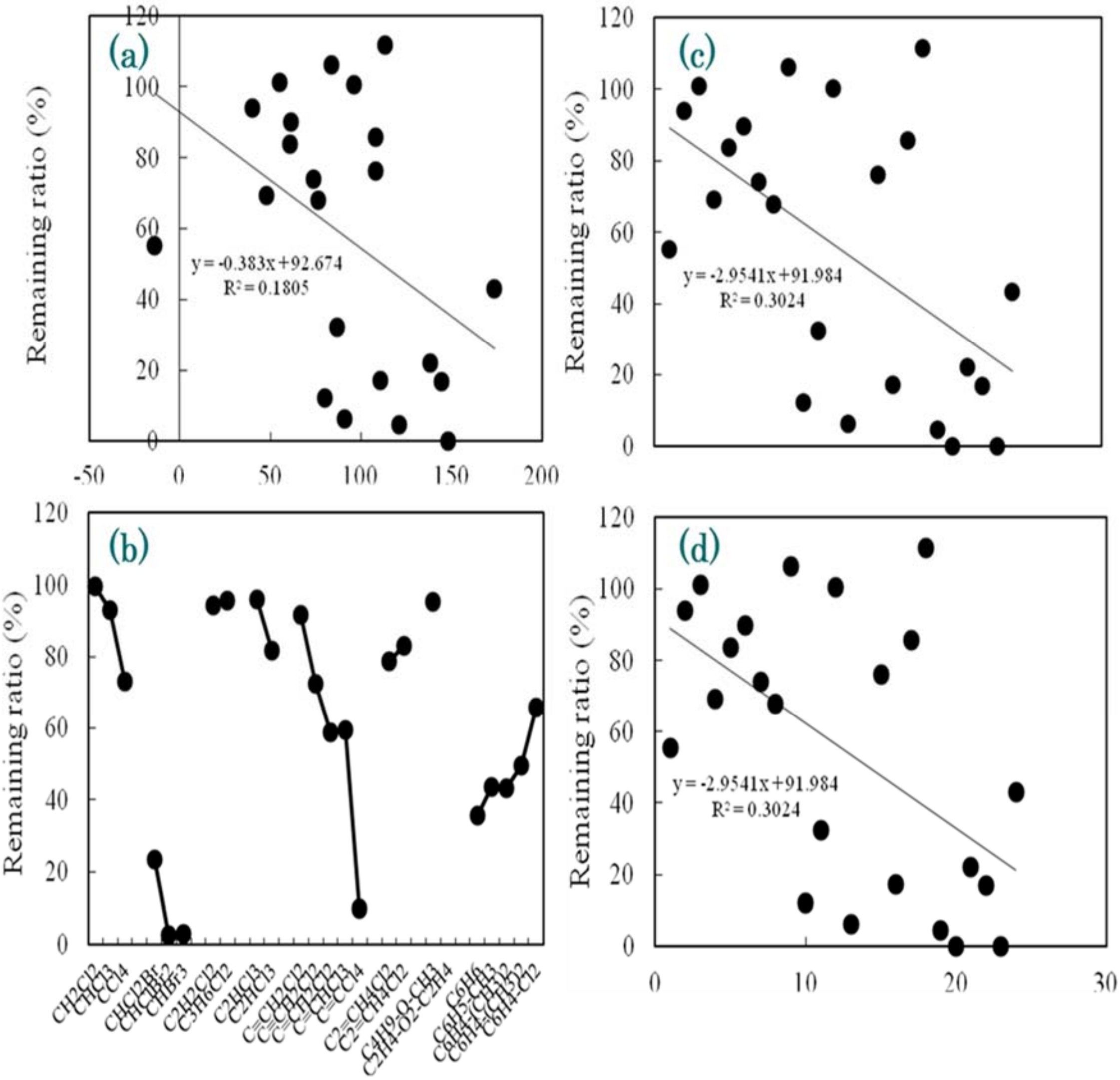


Figure 4-5 Relation between compound parameter and amount of the compound remaining after 4-h irradiation. (a) boiling point (°C), (b) chemical structure, (c) water solubility (g/100 g), (d) dielectric constant (F/m).

4.3.3 Decomposition Mechanism

Three mechanisms were considered for decomposition. One was direct scission of each bond by photo-irradiation. The black light (main wavelength: 365 nm) emits 328 kJ/mol energy that causes scission only of a C-Br bond like table 4-4 or a π bond. The sterilizeing lamp (wavelength: 254 nm) emits 471 kJ/mol of energy that causes scission of a C-Br bond, C-Cl bond, C-C bond, C-O bond, C-H (aliphatic and methane) bond, =C-H bond and π bond.

Table 4-4 Bonding energy at 25 °C (kJ/mol)

C-Br	285
λ = 365 nm	328
C-Cl	335
C-C	347
C-O	356
C-H (aliphatic)	412
C-H (methane)	416
=C-H	425
λ = 254 nm	471
C=C	610

The second possible mechanism is reaction of active substances generated from water upon photo-irradiation. Hydrogen and hydroxyl radicals are produced from water upon UVR irradiation at 185 nm (Eq. 1). However, these radicals are not produced at 254 nm.

$$H_2O \rightarrow \cdot H + \cdot OH \qquad (1)$$

The third possible mechanism is reaction of active substances generated by the TiO_2 photocatalyst and photo-irradiation. The TiO_2 photocatalyst is a nano-reaction field separation type, with a separate oxidation portion and reduction portion. Two-electron oxidation occurs in the hole of the photocatalyst (Eq. 2), producing H_2O_2 from water.

$$2H_2O + 2h^+ \rightarrow H_2O_2 + 2H^+ \qquad (2)$$

If dissolved O_2 exists in the water, the O_2 receives an electron and $\cdot O_2^-$ is produced per reaction 3. In addition, H_2O_2 is produced from reaction 4 and is converted to an OH radical via reaction.

$$O_2 + e^- \rightarrow \cdot O_2^- \qquad (3)$$

$$\cdot O_2^- + 2H^+ + e^- \rightarrow H_2O_2 \qquad (4)$$

$$H_2O_2 + e^- \rightarrow \cdot OH \qquad (5)$$

4.4 Conclusions

The photo-decomposition of VOCs generated by chlorination during water purification was investigated using a TiO_2 photocatalyst. The photo-decomposition of chemical substances that resist degradation in water is affected by contact with the surface of the photocatalyst. A thin reactor was used and the flow rate was high in this study, some compounds remained resistant to photo-decomposition.

Photocatalysts that are effective in sunlight are desirable. The photocatalyst used in this investigation was not effective upon exposure to black light. However, this photocatalyst has high durability, which allows the use of super-sonic wave irradiation. Thus, this photocatalyst can be used to produce integrated circuit wafer washing water.

Chapter Five - Production of active intermediates and decomposition behaviours of organic compounds in the ultraviolet ray/supersonic wave multiple reactions with TiO_2 photocatalyst

5.1 Introduction

The removal of the contamination with particle, organic and inorganic substances on the surface of IC wafer has become a serious problem attendant on the ultra-minute and high integrated semiconductor. At present, the washing with a reagent as acid, alkali or O_3 is mainly performed because the physical method as super-sonic wave (SSW) irradiation damages a semiconductor chip. But the washing method, which has a strong washing effect, takes a low cost and does not have the problem of wastewater treatment, is demanded.

The decomposition of chemical substance by the ultra-violet ray (UVR)/TiO_2 photocatalyst method was investigated. We could get the photocatalyst which was coated on the surface of carrier by the low temperature spraying method and was strong against physical force. Then, we produced the washing water, which was considered to contain radical and has a strong washing effect, by the UVR/SSW multiple reaction with a low temperature sprayed TiO_2 photocatalyst and investigated on the behavior of active intermediate. The photodecomposition-washing force of the active intermediate against CH_3OH and DMSO was also investigated.

5.2 Materials and methods

5.2.1 Reagents

1/40N $KMnO_4$ solution was prepared by the dilution of 1/5N $KMnO_4$ solution for volumetric analysis obtained from Wako Pure Chemical Industries. KI for oxidant analysis, citric acid for food additive and soluble starch (the highest quality reagent) were obtained from Hayashi Pure Chemical Industries, Wako Pure Chemical Industries and Katayama Chemical Industries, respectively. 1/100N Na_2S_2O4 solution was prepared by the dilution of 1/10N $Na_2S_2O_4$ solution for volumetric analysis obtained from Wako Pure Chemical Industries. The other reagents were the highest quality reagent.

CH_3OH for pesticide residue/PCB test and HCOOH were obtained from Kanto Kagaku and Kishida Chemical, respectively. DMSO (99.7% <), 1-methanesulfinate (MSFIA) (85%) and 2-methanesulfonic acid (MSFOA) were obtained from Merck, Aldrich and Kanto Kagaku, respectively. The ultra-pure water was purified using a Japan Millipore Milli-Q Element A10 (18.8 MΩ cm).

5.2.2 TiO_2 Photocatalyst

The TiO_2 photocatalyst, which was a nano-reaction field separation type by doping Fe, was used. The photocatalyst was coated on the surface of aluminum fiber (10 cm × 10 cm × 3-5 mm) by the low temperature spraying method and has high durability. As the coating was done at low temperature, the crystal structure was an anatase type which is generally said to have better decomposition ability against organic compound.

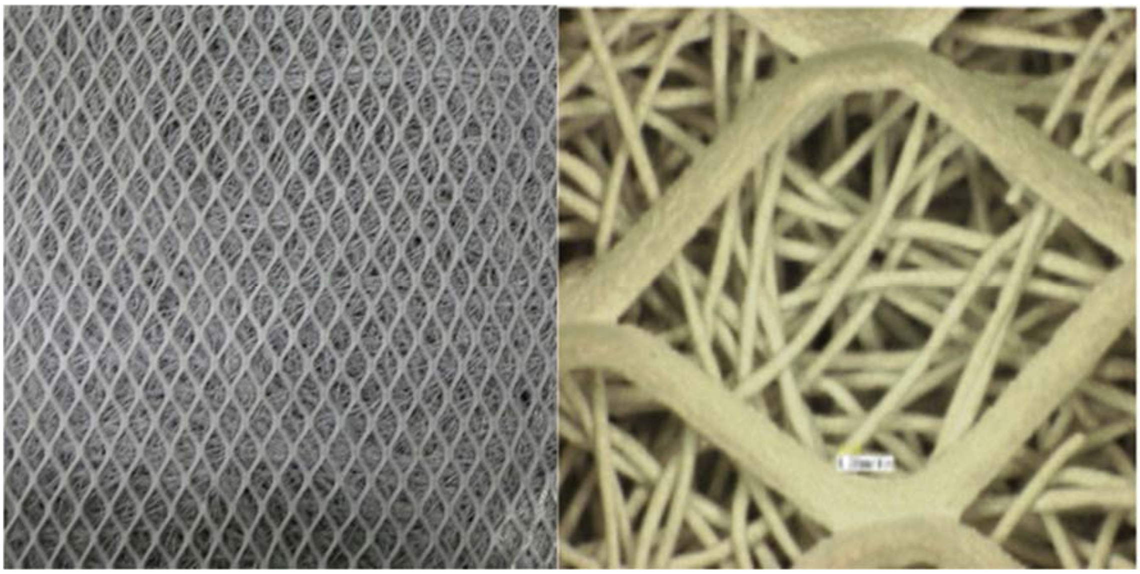


Figure 5-1 Photocatalyst was coated on the surface of aluminum fiber

5.2.3 Instruments

UVR (photocatalyst) /SSW irradiation apparatus was shown in figure 5-2. UVR sterilize lamp was a Zensui UV clean-13 (13 W, 254 nm, irradiation surface was about 320 cm^2). UVR sterilize lamp has a tight lid of aluminum board (31 cm × 25 cm) like figure 5-3. The reactor (24.6 cm × 18.6 cm × 24.2 cm) was made of stainless steel and a Honda Electronics W-357HP-S SSW dispatchor (1 MHz) is placed the bottom of reactor like figure 5-4. Pump was a Surpass Industry Teflon bellows pump Model BP-300 and a NRK chemipump. UVR intensity was measured on the surface of UVR sterilize lamp with a Topcon Technohouse UVR-2.

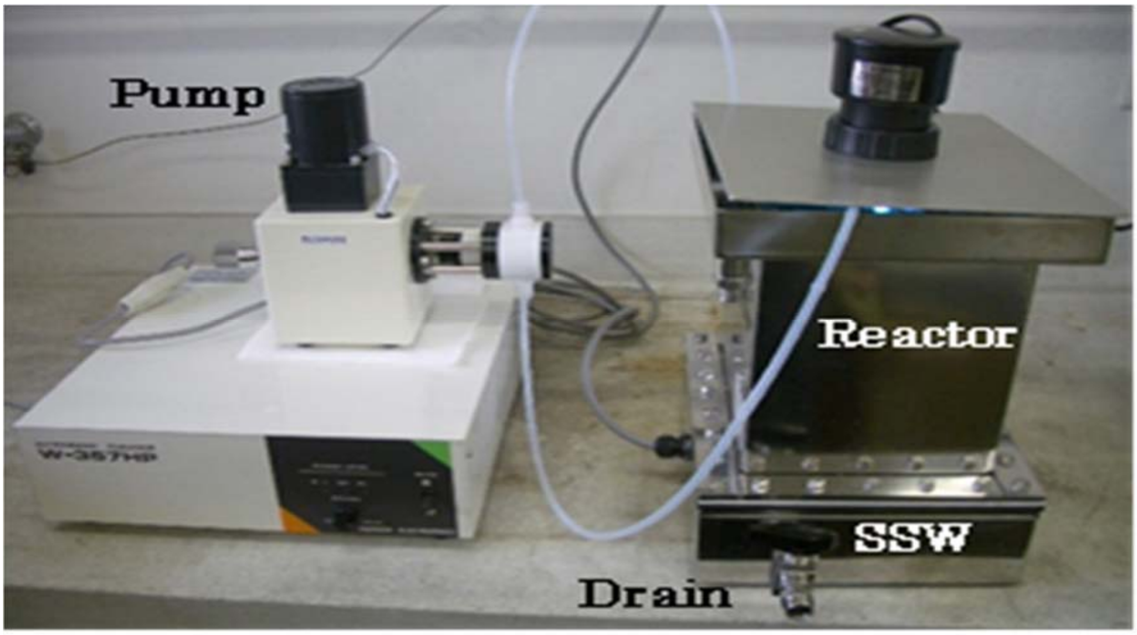


Figure 5-2 Apparatus for multiple photoreactions

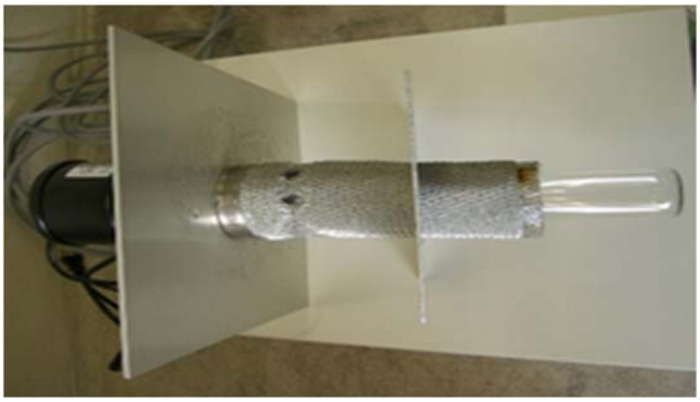


Figure 5-3 UV lamp with photocatalyst cover

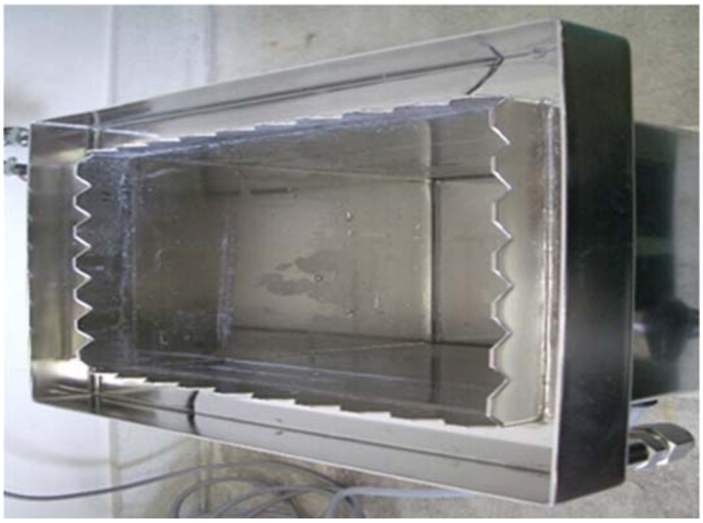


Figure 5-4 Reactor tank

Total organic carbon (TOC) analyzer was a Shimadzu autosampler ASI-V/TOC-VCSH. Ion chromatograph was a Nippon Dionex autosampler AS/ion chromatograph ICS-1500/autosupressor SRS/multipurpose chromatography interface UCI-50/UV-visible absorption spectrophotometry detector UVD-510. PH meter and electric conductivity (EC) meter were a Horiba D-13 and a Toa Electronics CM-14P, respectively.

5.2.4 Thermal elution from photocatalyst

The thermal eluates from the photocatalyst were investigated because the water temperature became at max 70 °C after the reaction of 4 h. The photocatalyst was placed in 500 ml of ultra-pure water and heated at 80 °C for 30 min. Further, the photocatalyst was heated at 100 °C for 30 min and cooled. PH, EC, iodine consumed and $KMnO_4$ consumed of the water were measured.

5.2.5 UVR/SSW irradiation

The sample water was circulated with a pump. The reacted water sample was periodically placed in 500 ml of PFA bottle and immediately measured. The each condition was as follows. Initial water temperature: 15-20 °C; flow rate: 500 ml/min; UVR intensity: 4.5 mW/cm^2; SSW intensity: 500 W (ultra-pure water and DMSO), 350

W (CH_3OH); sample volume: 10 L; initial concentration: 0.1 ml/L (CH_3OH), 100 mg/L (DMSO).

4.2.6 Analytical Methods

Each item was analyzed by the Testing Methods for Water Supply. PH and EC were measured using a pH meter and an EC meter, respectively. Oxidizing substances were measured by the titration method with 0.01 N $Na_2S_2O_4$ solution for free I_2. H_2O_2 was measured by the KMnO4 method. TOC was measured by the combustion-oxidation method. HCOOH, DMSO, MSFIA and MSFOA were measured by the ion chromatography.

5.3 Results and discussion

5.3.1 Thermal elution from photocatalyst

By heating at 80 °C for 30 min, pH and EC changed 5.02 to 5.73 and 2.84 to 3.63 μS/cm, respectively. Further, pH and EC changed 5.11 to 6.21 and 2.87 to 3.11 μS/cm, respectively by heating at 100 °C for 30 min. Iodine consumed and $KMnO_4$ consumed were not detected.

The influence of thermal elution can be negligible because pH and EC did not change by heating of same photocatalyst at 80 °C for 30 min again.

5.3.2 Reaction of ultra-pure water

The results of temperature and pH are shown as figure 5-5. The water temperatures 4-h after in UVR and SSW irradiation were 21-23 °C and 67-68 °C, respectively. PH decreased by SSW irradiation (mainly H^+ was produced) and became a little higher by UVR irradiation. With the photocatalyst, pH became higher by both UVR and SSW irradiation (mainly OH^- was produced). As the influence of SSW was stronger, pH was decreased by UVR/SSW irradiation. With the photocatalyst, pH increased till 2-h (increase of OH^-) and decreased after 2-h by the influence of SSW (increase of H^+).

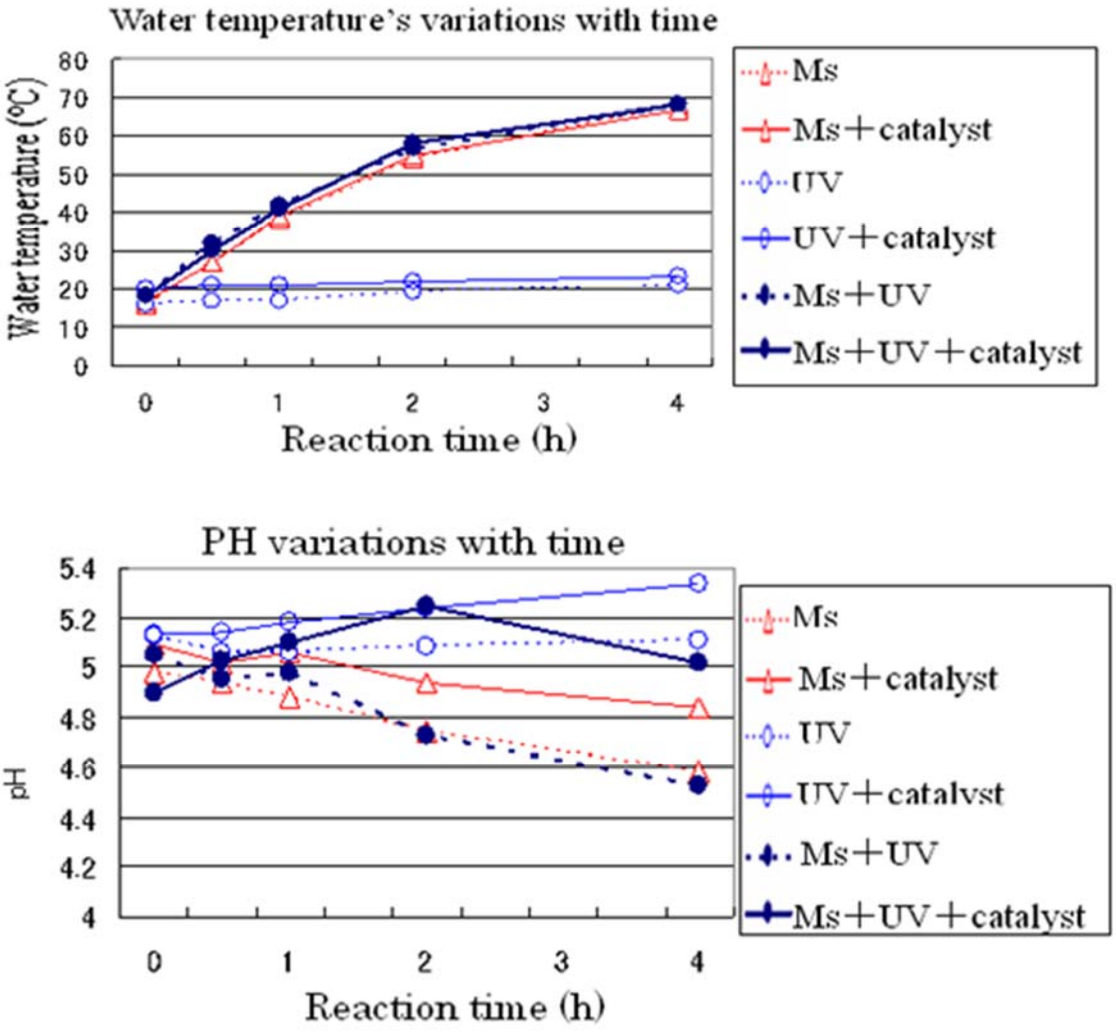


Figure 5-5 Changes of temperature and pH. Flow rate: 500 ml/min; UVR intensity: 4.5 mW/cm^2; SSW intensity: 1 MHz, 500 W.

Figure 5-6 shows the results of EC and iodine consumed. EC did not increase by only UVR irradiation but increased by SSW irradiation (increase of H^+). EC slightly increased by UVR/SSW irradiation than the sum of EC by each irradiation and increased without the photocatalyst. It was considered that more hydroxyl radical was produced with photocatalyst and existed during EC measurement by SSW function (every pH with photocatalyst was higher and more OH^- existed).

Iodine consumed shows the oxidizing substances such as O_3, H_2O_2 and radical. They are shown in Eq. 1, 2, 3. Iodine consumed was detected in SSW irradiation and was not detected in only UVR irradiation. Iodine consumed without the photocatalyst was larger than with it in case of only SSW irradiation. The effect of the photocatalyst was observed in UVR/SSW irradiation but the iodine consumed became smaller than in only SSW irradiation after 4-h.

$$2 \cdot OH + 2I^- \rightarrow I_2 + 2OH^- \qquad (1)$$

$$O_3 + 2I^- + H_2O \rightarrow I_2 + 2OH^- + O_2 \qquad (2)$$

$$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O \qquad (3)$$

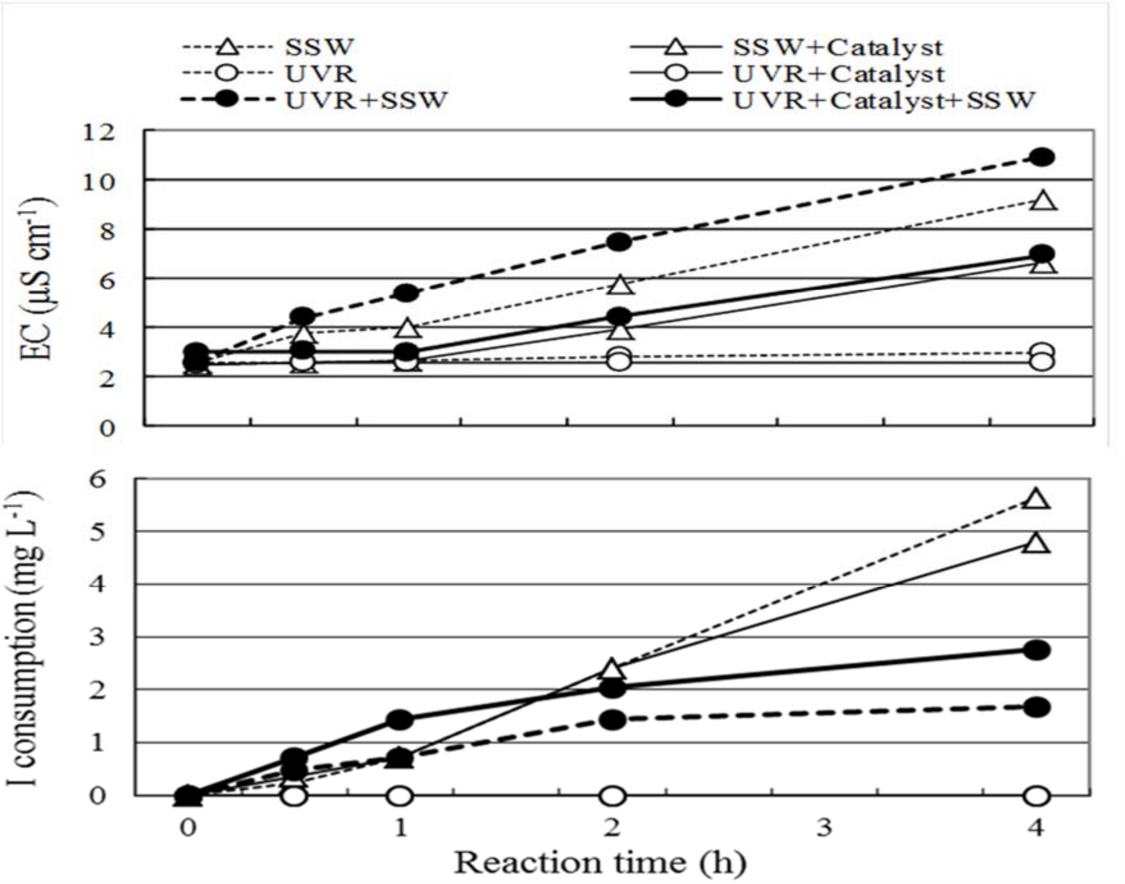


Figure 5-6 Changes of EC and iodine consumed. Flow rate: 500 ml/min; UVR intensity: 4.5 mW/cm^2; SSW intensity: 1 MHz, 500 W.

$KMnO_4$ consumed was measured to examine H_2O_2 production. $KMnO_4$ reaction with H_2O_2 is shown in Eq. 4. However, the same periodical changes as iodine consumed were observed. The result was like figure 5-7

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5O_2 + 8H_2O \qquad (4)$$

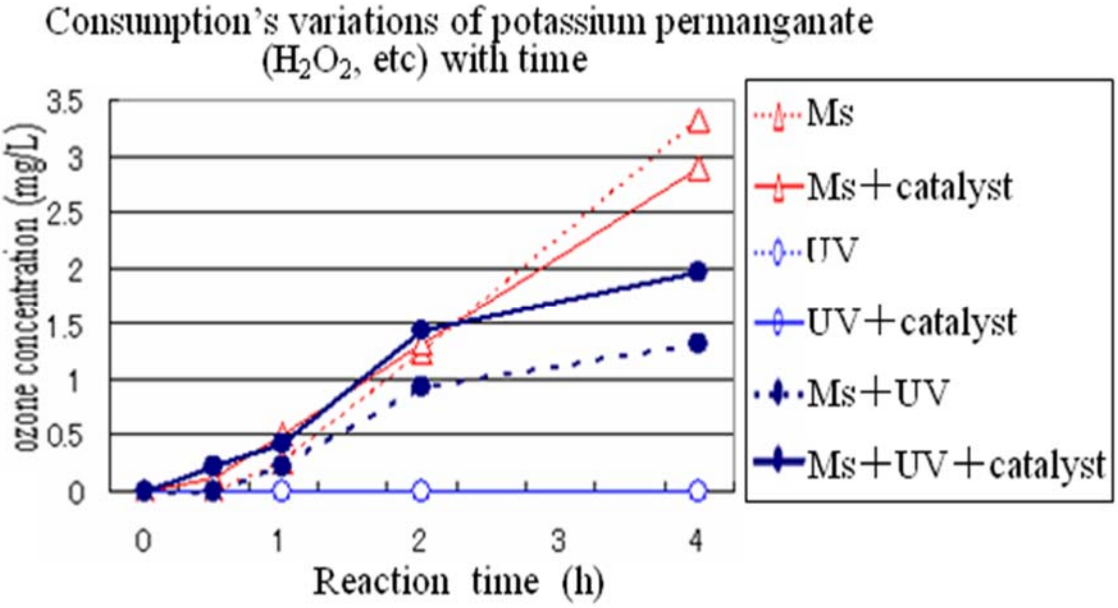


Figure 5-7 Changes of potassium permanganate. Flow rate: 500 ml/min; UVR intensity: 4.5 mW/cm^2; SSW intensity: 1 MHz, 500 W.

5.3.3 Consideration of oxidizing substances produced

Hydrogen and hydroxyl radical are produced from water at 185 nm of UVR irradiation as the photochemical reaction 5. Though those radicals are not produced at 254 nm, hydroxyl radica is produced as the reaction 6 if H_2O_2 was produced.

$$H_2O \rightarrow \cdot H + \cdot OH \qquad (5)$$

$$2H_2O_2 \rightarrow OH^- + \cdot OH + HO_2^- + H^+ \qquad (6)$$

This TiO_2 photocatalyst is that of nano-reaction field separation type and an oxidation part and a reduction part are separated. Two electrons oxidation occurs in the hole of the photocatalyst as the reaction 7 and H_2O_2 is produced from water.

$$2H_2O + 2h^+ \rightarrow H_2O_2 + 2H^+ \qquad (7)$$

If dissolve O_2 exists in water, O_2 receives an electron and $\cdot O_2^-$ is produced as the reaction 8. Further, H_2O_2 is produced as the reaction 9 and is converted to $\cdot OH$ as the reaction 10.

$$O_2 + e^- \rightarrow \cdot O_2^- \qquad (8)$$

$$\cdot O_2^- + 2H^+ + e^- \rightarrow H_2O_2 \qquad (9)$$

$$H_2O_2 + e^- \rightarrow \cdot OH \qquad (10)$$

By SSW irradiation, hydrogen and hydroxyl radical are also produced by the thermal decomposition of H_2O as the reaction 5. If dissolve O_2 exists in water, O・ is also produced as the reaction 11.

$$O_2 \rightarrow 2O\cdot \qquad (11)$$

The active intermediates produced by UVR (photocatalyst)/SSW irradiation are considered as H_2O_2, H^+, OH^-, HO_2^-, ・H, ・OH and O・ from these reactions. H_2O_2 produced is converted to ・OH as the reactions 6 and 10. If H_2O_2 existed, it should be detected because its self-decomposition rate was later. Both of iodine consumed and $KMnO_4$ consumed were not detected in case of only UVR irradiation (the reactions 7 and 9). Further, both periodical changes were exactly alike. Therefore, $KMnO_4$ consumed did not show H_2O_2 but showed the oxidizing substances which were stronger than $KMnO_4$ such as radical.

Water temperature, pH, EC, iodine consumed and $KMnO_4$ consumed were measured within several minutes out of the reaction system. Usually radical can not be measured because it disappears at µs. However, radical exists for several minutes by the effect of micro- or nano-bubble of SSW irradiation. In fact, iodine consumed and $KMnO_4$ consumed were not detected in case of only UVR irradiation. Therefore, it was considered that some radicals were contained in the oxidizing substances in the UVR (photocatalyst)/SSW irradiation system and the photocatalyst promoted the radical production.

5.3.4 Reaction of CH_3OH

The water temperature 4-h after in UVR and SSW irradiation was 19 °C and 49-55 °C, respectively. PH more decreased by SSW irradiation than by UVR irradiation and further decreased by UVR/SSW irradiation. With the photocatalyst, pH became higher. EC did not increase by only UVR irradiation but increased by SSW irradiation. EC slightly increased by UVR/SSW irradiation than the sum of EC by each irradiation and increased without the photocatalyst.

Iodine consumed was detected in SSW irradiation and was not detected in only UVR irradiation as in case of ultra-pure water. Iodine consumed without the photocatalyst was larger than with it in cases of both only SSW and UVR/SSW irradiation.

Figure 5-8 shows the changes of TOC and HCOOH. TOC decrease was large UVR/SSW>SSW>UVR irradiation in turn and the effect of photocatalyst was observed in all cases. Eight % of CH_3OH was converted to CO_2 4-h after. HCOOH, an oxidation product of CH_3OH, was not detected in only UVR irradiation but detected in SSW irradiation. The synergism with UVR irradiation was observed and HCOOH production decreased with the photocatalyst. Table 5-1 shows the amounts of other products 1-4 4-h after. These products were not detected in only UVR irradiation but detected in SSW irradiation. Generally, their amounts tend to increase without the photocatalyst.

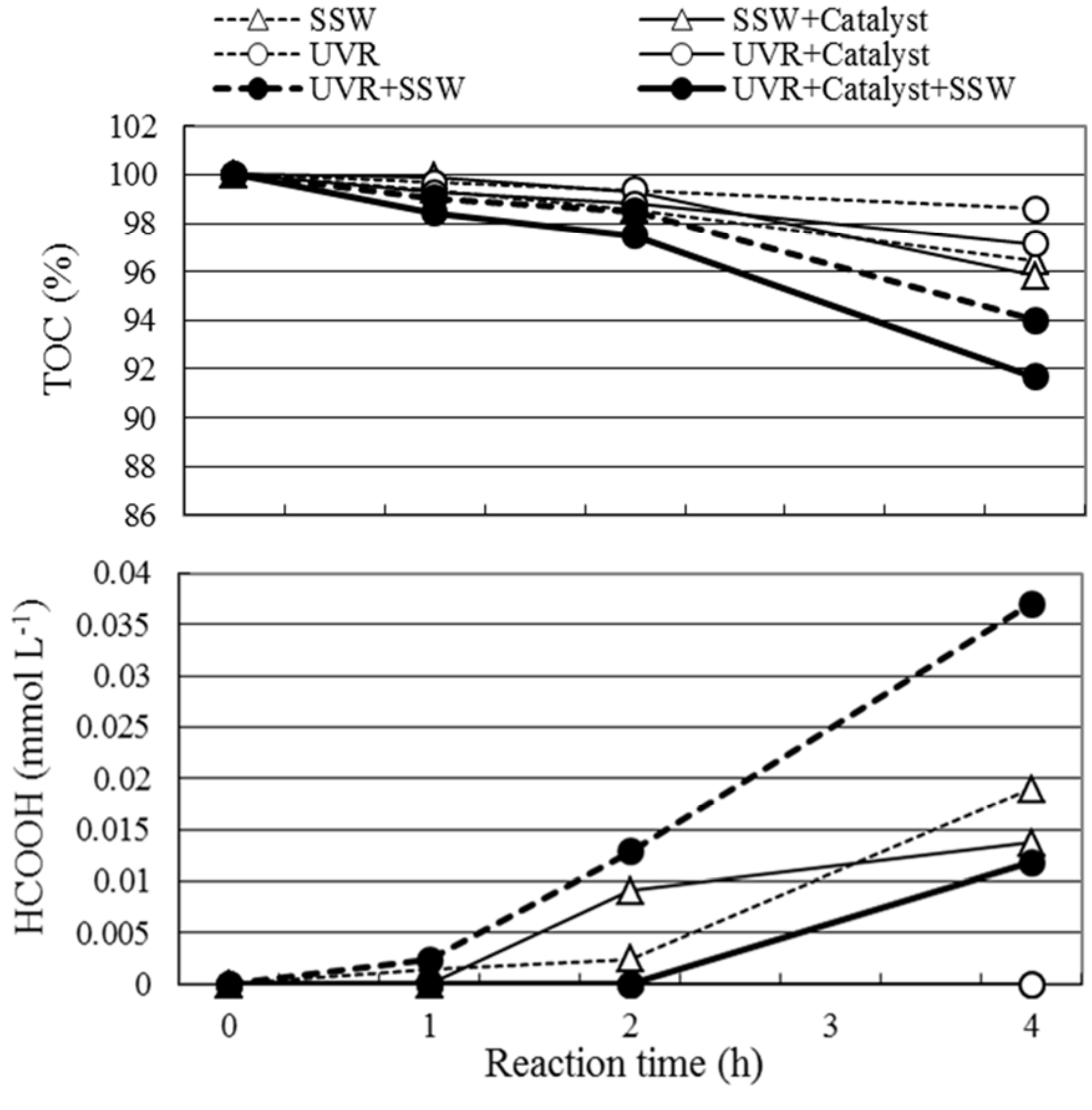


Figure 5-8 Changes of TOC and HCOOH. Initial concentration of CH_3OH: 0.1 ml/L; flow rate: 500 ml/min; UVR intensity: 4.5 mW/cm^2; SSW intensity: 1 MHz, 350 W.

Table 5-1 Amounts of products 1-4 after 4-h reaction

	Product 1	Product 2	Product 3	Product 4
	(μS min)		(mAU min)	
SSW	0.019	0.021	0.39	0.43
SSW + Catalyst	0.015	0.002	0.30	0.27
UVR	-	-	-	-
UVR + Catalyst	-	-	-	-
UVR + SSW	0.012	0.014	0.32	0.78
UVR + Catalyst + SSW	0.014	0.008	0.33	0.39

5.3.5 Reaction of DMSO

The water temperatures 4-h after in UVR and SSW irradiation were 17-24 °C and 66-69 °C, respectively. PH more decreased by SSW irradiation than by UVR irradiation and further decreased by UVR/SSW irradiation. With the photocatalyst, pH became higher. EC increased by SSW irradiation. EC slightly increased by UVR/SSW irradiation than the sum of EC by each irradiation and increased without the photocatalyst. Iodine consumed was detected in SSW irradiation and also detected slightly in only UVR irradiation.

Change of DMSO is shown as figure 5-9. DMSO decrease was a little in every case and the effect of the photocatalyst was not observed clearly. MSFIA, an oxidation product of DMSO, was detected in SSW irradiation but slightly detected in only UVR irradiation. Amount of MSFIA decreased by UVR/SSW irradiation or with the photocatalyst. In case of MSFOA, an oxidation product of DMSO, the synergism by UVR/SSW irradiation was observed but its amount decreased with the photocatalyst. Table 5-2 shows the ratios of the products of DMSO after 4-h. The effect of the photocatalyst, which was also effective in near-visible area, could not be shown sufficiently because the wave length of the UVR sterilize lamp was only 254 nm.

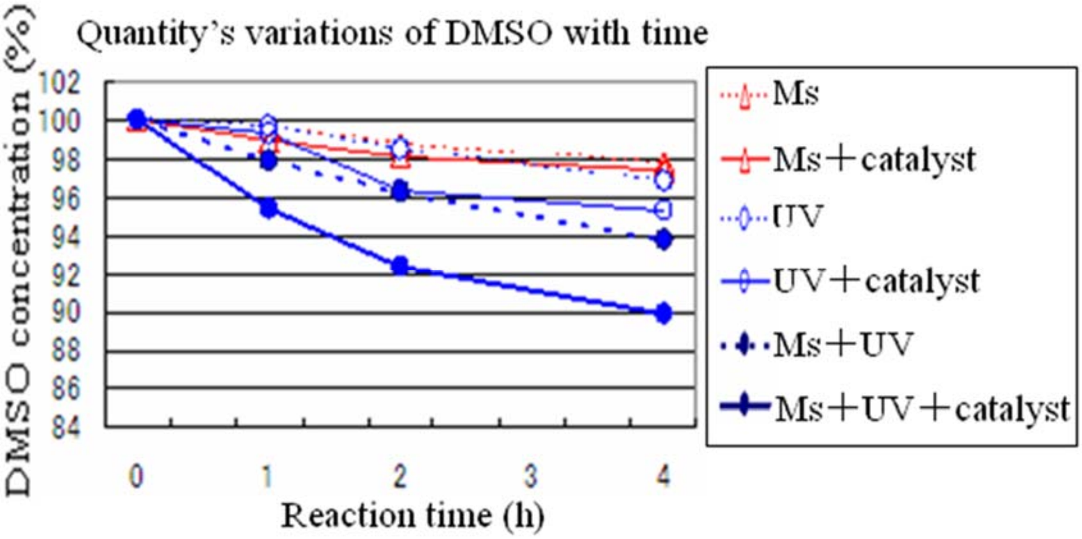


Figure 5-9 Changes of DMSO. Initial concentration of DMSO: 0.1 ml/L; flow rate: 500 ml/min; UVR intensity: 4.5 mW/cm^2; SSW intensity: 1 MHz, 350 W.

Table 5-2 Ratios (%) of reaction products of DMSO after 4-h reaction

	DMSO	MSFIA	MSFOA	Others
SSW	90.5	0.1	8.5	0.9
SSW + Catalyst	93.2	0.2	6.6	0
UVR	95.4	0.7	0.8	3.1
UVR + Catalyst	97.2	0.2	2.6	0
UVR + SSW	81.3	0.6	18.1	0
UVR + Catalyst + SSW	90.3	0	9.2	0.5

5.4 Conclusions

The The oxidizing substances, which oxidizing powers were stronger, were produced by the decomposition of water using the UVR/SSW multiple reaction with TiO_2 photocatalyst. Amount of the products increased by UVR/SSW irradiation and the effect of the photocatalyst was also observed. As the photocatalyst has high durability, SSW irradiation can be used. We consider that the oxidizing substances contain some radical and the radical can exist in nano- or micro-bubble generated by SSW irradiation if they part from the reactor. As radical has stronger oxidizing power and it does not have the problem of wastewater, the water can be used as IC wafer washing water. Further, the utilization of the water would expand to other fields by clearing up the kind of radical.

The decomposition behaviors of CH_3OH and DMSO were investigated using the reaction. Max. 8.0% of CH_3OH was converted to CO_2 4-h after and 5 kinds of intermediates containing HCOOH were produced. Max. 18.7% of DMSO was decomposed 4-h after and MSFIA and MSFOA were produced. The effects of the UVR/SSW multiple reactions and the photocatalyst were also observed in these decomposition behaviors.

Hereafter, the washing effect of the produced water against the contamination on the surface of IC wafer must be investigated.

Chapter Six - Discusses the generation of hydroxyl radical in the process of ozone/ultraviolet ray/supersonic wave multiple reactions with TiO_2 photocatalyst, and quantitative and qualitative analysis of generated hydroxyl radical with chemiluminescence and other methods.

6.1 Introduction

The hydroxyl radical is often referred to as the "detergent" of the troposphere because it reacts with many pollutants, often acting as the first step to their removal. And demand has been increasing in recent for treatment of wastewater containing recalcitrant organic matter such as dioxins or agricultural chemicals or for cleaning of some heavy metals or oil and so on, which are not able to be treated by traditional treatment technology (such as chlorine or ozone). Recently, semiconductor industry researchers have investigated the use of hydroxyl radical for wafer-cleaning, because hydroxyl radical has high oxidation potential, it is 10～10000 times higher than ozone. Now our objective of this study is the development of cleaning semiconductor device using hydroxyl radical water generated by "O_3-water/UV/MS/TiO_2" to lower chemical consumption and disposal costs as well as to improve cleaning efficiency and reduce the damage from physical process. We expect this method can be used for cleaning semiconductor device as environment-friendly as we can.

To improve cleaning efficiency, it is necessary that hydroxyl radical was confirmed to be formed from the wafer cleaning solutions. Meanwhile for theory of wafer cleaning using hydroxyl radical, it also needs to be clarified extensively. So, we need to confirm the generation, quantitative and qualitative analysis of hydroxyl radical in the process of ozone/ultraviolet ray/supersonic wave multiple reactions with TiO_2 photocatalyst.

But, because hydroxyl radical has an extremely short lifetime, it is difficult to determine it directly. In recent studies, several methods have been developed to detect hydroxyl radical, including electron spin resonance (ESR), High Performance Liquid Chromatography (HPLC), laser-induced fluorescence (LIF), colorimetric spectrophotometry, a radiocarbon method, and quantitative analysis of hydroxyl radical by oxidating CO to CO_2. However, these reported methods have lots of limitations for actives species determination. In this paper, we describe a new method for detecting hydroxyl radical scavenging capacity based on chemiluminescence and flow injection analysis. Hydroxyl radical was generated by the fenton reaction and the device of "O_3-water/UV/MS/TiO_2". The proposed method is a rapid, selective, and accurate procedure for the study of hydroxyl radical scavenging capacity by chemiluminescence.

6.2 Hydroxyl radical generation system

Our experiment expects to generate large quantity of hydroxyl radical water by the technology comprehensively using ozone, ultraviolet, ultrasonic and high light sensitive titania nanotube photocatalyst. And then achieve conspicuous clean effects on various metal contaminants. First, generate 6~8 ppm ozone water from ozone water generating equipment, and let the ozone water generated flow into the hydroxyl radical generation device which is for the experiment. The device is shown as figure 6-1. The inner sides of the experiment device consists of TiO_2 photocatalyst thin-film coating fused on the quartz glass surface, illuminated by eight low-pressure mercury lamp (wavelength is 185 nm, 254 nm, 305 nm and 365 nm), and then the bottom of the device sets low-megahertz ultrasonic. This device can produce high-concentration hydroxyl radical that is strongly able to oxidize and decompose. Hydroxyl radical can make metal impurities completely ionized and dissolved by water, reaching the purpose of cleaning and removing the metal impurities.

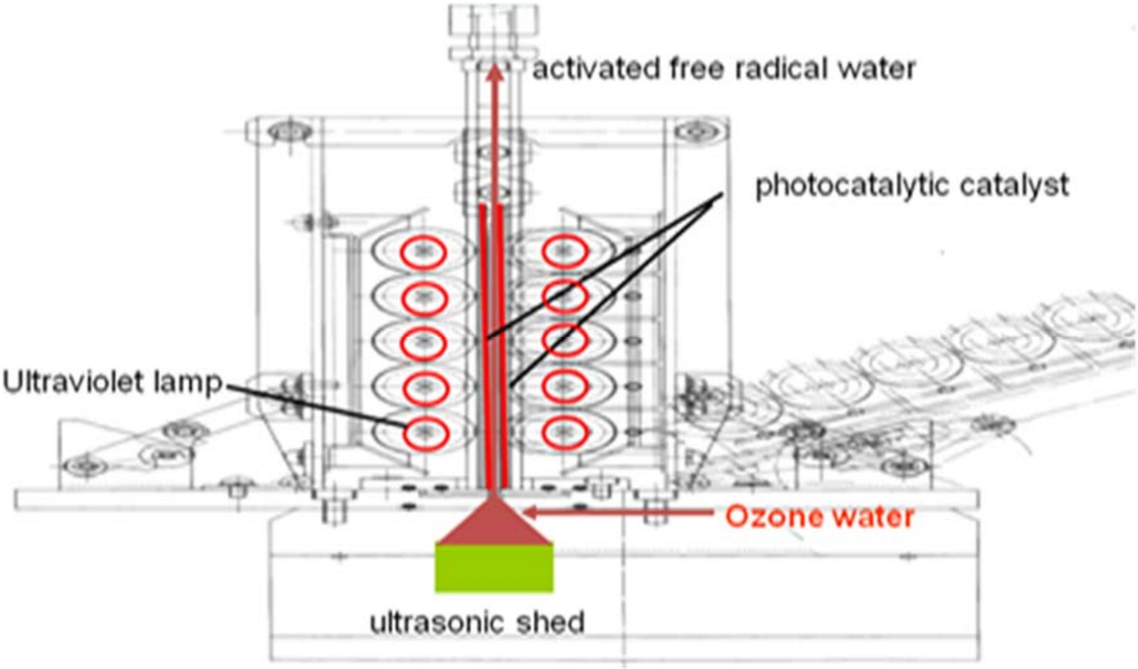


Figure 6-1a Mobile hydroxyl radical generation device diagram

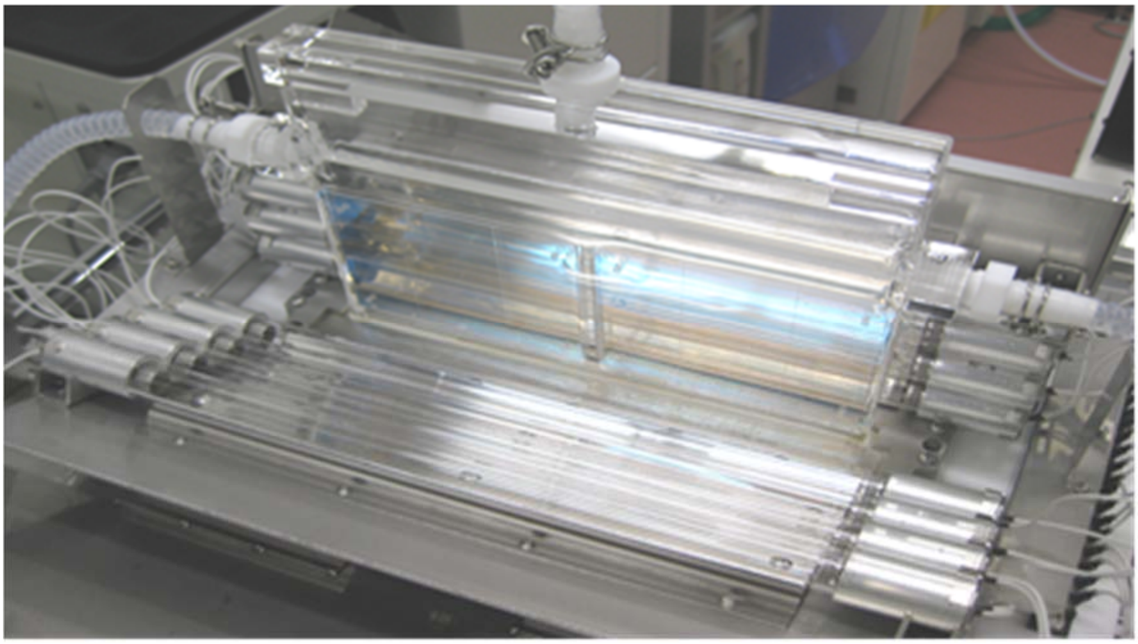


Figure 6-1b Mobile hydroxyl radical rinse water (O_3-water/UV/MS/ TiO_2) equipment

OH radical water production systems operation:

1. Check power cord, piping, cock, etc.
2. Each device is turned off. Check that oxygen regulator of ozone water generation device is closed.
3. Apparatus of ultraviolet irradiation for water treatment. Open its cover of stainless steel so that we can see the water level in the synthetic quartz glass. —— touch lamp,

glass case and rubber with cotton gloves (if touched with bare hands, we should wipe with acetone, etc.)

4. Oxygen gas (purity more than 99.9%) open the main valve (turn left), turn the regulator valve to 0.1MPa, then open the valve of ozone water generation apparatus (turn left). — — ahead of the ultra-pure water, make the oxygen gas inflow (when to stop, ultrapure is the first)

5. Slowly open the oxygen gas flow control valve which is on the ozone water generation equipment. And fit that oxygen gas pressure is 0.1MPa, flow is 2.0L/min.

6. Turn right the three-way cock of ultra-pure water to 90°,while watching the level of raw materials water flow meter and glass case of ozone water generation equipment (overflow or leakage), regulate a valve to set water flow 1.0L/min or less.

7. Turn on the main switch of ozone water generation equipment, make sure that the monitor of ozone-water concentration get countdown and back from 300 to 0. (Warm up 5 minutes.)

8. Adjust the output mode selector switch to control, set the ozone generator output controller to 00.

9. Set the main switch to ozone, and set the controller of output ozone generator (up to 0-99%, when we want to set 100% driver, we can adjust the output mode selector switch to FULL).

When using ultrasound:

· When power switch of ultrasonic oscillator is OFF, set the upper limit (green) of the current meter is 1.4A; low limit (red) is 0.5A.

· Avoid boiling, check the valve noise of the apparatus of ultraviolet irradiation for water treatment and ozone water generation equipment, and set the power switch to ON state.

· Make sure that OPER lamp light is on, make the current value maximum with tuning knob (but it causes damage, as soon as it is more than 1A, so power volume must be from 0.7 to 1A).

· If an alarm is sounded or when to stop (liquid supply is shortage, current is lack or over-current) the power switch will be OFF state.

When using UV

· Take care the mounted lamps and stainless steel cover, UV-blocking, ventilation of ozone generation on the apparatus of ultraviolet irradiation for water treatment, set the power switch to ON state (light stable is about 2 or 3 minutes).

· Ambient temperature is 15-35 °C, be careful that there is no condensation.

· When you stop the power switch to OFF state. (ON, OFF is not often)

10. When stop the ozone water generating device, turn the main switch to on, make sure that the monitor of concentration of ozone water is back to zero (take about 5 minutes).
11. Set output controller of ozone generator to 00.
12. Set the main switch to off, and stop the electromagnetic valve, discharge ozone water from inside of the unit.
13. Fully close oxygen gas flow control valve (clockwise) to terminate the operation.
Above-mentioned contents are hydroxyl radical water production systems operation:
Under different conditions, respectively take a certain amount rinse water samples from the mobile hydroxyl radical rinse water (O_3-water/UV/MS/TiO_2) equipment, immediately measure the ozone concentration of all samples with portable ozone monitor. Then respectively get 100 ml samples with graduated cylinder again, taken the amount and concentration of oxidants by KI method. At last according to the experiment's dates, calculate the concentration of new generated oxidants, and then draw the graph of rate of oxidants concentration such as figure 6-2.

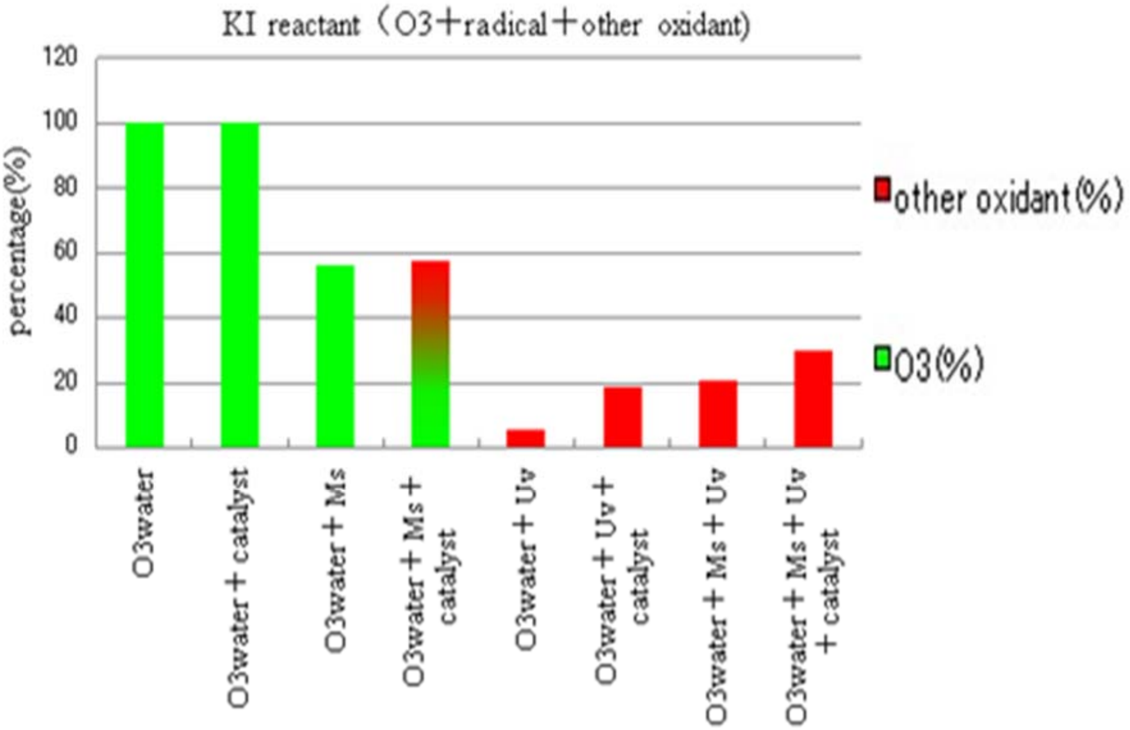


Figure 6-2 Generated oxidant quantities' percentage

Put the reactive oxygen species rinse water into a container such as beaker, after putting the KI into the same beaker. Then the iodine got free from potassium iodide, and the color turned into yellow. Got this colored solution into a graduated cylinder 100cc to take measure, and transferred the colored solution into the new container, then added 10% citric acid (citric acid monohydrate 20g dissolved in 180ml pure water) 5cc with syringe. Had the purple colored reaction between starch and iodine, as soon as put 1ml starch solution into a beaker with colored solution (put 1g soluble starch into 200ml pure water, then the solution is heated to dissolve). Took 0.01 N sodium thiosulfate with burette, then dripped sodium thiosulfate into purple colored solution then stirred frequently to cause reaction between sodium thiosulfate and iodine. The reaction could make the color disappear. A certain amount of sodium thiosulfate was dropped before the color disappeared completely, we could calculate the concentration of reactive oxygen species. Iodine consumed shows the oxidizing substances such as O_3, H_2O_2 and radical. They are shown in Eq. 1, 2, 3.

[Ozone water concentration (ppm)] = [dripping sodium thiosulfate (cc) - blank] × 0.24 (mg) / 0.1

$$O_3 + 2I^- + H_2O \rightarrow I_2 + 2OH^- + O_2 \qquad (1)$$

$$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O \qquad (2)$$

$$2 \cdot OH + 2I^- \rightarrow I_2 + 2OH^- \qquad (3)$$

When there is only the UV radiation, the ozone disappeared entirely. In addition, new reactive oxygen species can be generated by our methods. Meanwhile, photocatalyst had a great effect on the decomposition of ozone and the generation of new reactive oxygen species. At the last, compared with the UV effect alone, UV worked best when used in conjunction with ultrasound. The following test needed to prove the generation of hydroxyl radical.

6.3 Material and methods

6.3.1 Instruments

PH meter, electric conductivity meter (EC meter) and oxidation-reduction potentiometer (ORP meter) were a Horiba D-13, a Toa Electronics CM-14P and a Toa Electronics YK-23RP, respectively. O_3 analyzer and chemiluminessensor were an Applics OM-101P-30 and an Atto AB-2200 PSN, respectively. Atomic absorption spectrometer (AAS) was a Varian AA240 FS. Gas chromatograph/mass spectrometer (GC/MS) was an Agilent Technologies 7683B series injector/7890A GC system/5975C inert XL EI/CI MSD with triple-axis detector.

6.3.2 Reagents

Potassium iodide for oxidant analysis, citric acid, luminol, chlorogenic acid, DL-tartaric acid (98% <), soluble starch, 1N $KMnO_4$ solution for volumetric analysis, silver sulfate for CODMn analysis, benzene (benzene 5,000), ethylbenzene, o-xylene, o-cresol, benzophenone, bromobenzene and pyridine were obtained from Wako Pure Chemical Industries. Zn powder (99.999%, 100-200 mesh), Fe powder (99.5%, 6.5 μm), Ni powder (99.9%, 3-7 μm), Cu powder (99.9%, -300 mesh) and Ag powder (99%, -325 mesh) were obtained from Mitsuwa Chemical Reagent. 1 N $Na_2S_2O_4$ solution and 1/40 N sodium oxalate solution were obtained from Kanto Chemical. Other reagents were special grade reagents. The ultra-pure water was purified using a Japan Millipore Milli-Q Element A10 (18.8 MΩcm).

6.4 Identification of hydroxyl radical

6.4.1 Reaction with metals

Each 0.05 g of Zn, Fe, Ni, Cu and Ag powder was mixed with 200 ml of the reacted water sample in 300 ml of separatory funnel. Each ionized metal was filtrated using 1 μm of GFP after 2 days and measured.

6.4.2 Chemiluminescence

The reacted water sample was reacted with luminol and chlorogenic acid and measured.

6.4.3 Reaction with organic compounds

The reacted water sample was reacted with DL-tartaric acid and soluble starch and each CODMn was measured.

Each 1 g of benzene, ethylbenzene, o-xylene, o-cresol, benzophenone, bromobenzene and pyridine was mixed with 200 ml of the reacted water sample in 300 ml of separatory funnel and sufficiently reacted. The reacted solution was extracted with each 50 ml of dichloromethane twice. The extracted solution was dehydrated with anhydrous Na2SO4, concentrated to 2 ml and the OH compounds produced were identified.

6.5 Analytical methods

6.5.1 Luminescence-based techniques for the quantitative and qualitative analysis of hydroxyl radical

Hydroxyl radical plays a crucial role in a wide variety of chemical and biological systems. During the past several years, it is generally believed that human diseases caused by hydroxyl radical, as it is having high reactivity and not selective due to the presence of unpaired electron. Hydroxyl radical, who is regarded as non-selective radical species, is able to attack any molecule in their vicinity in order to balance their unpaired electron configuration. Recently due to increase use of various chemicals and persistent chemicals, and some of them react together to form new refractory organic compounds in the environment, therefore, hydroxyl radical is expected to contribute to the development of environmental treatment, because it is possible to degrade almost organic compound to carbon dioxide, water and no risk of secondary pollution by by-product, even chemicals that are otherwise very difficult to degrade. Hydroxyl radical is also referred to as the detergent in the atmosphere through reactions with many pollutants, such as CO, CH_4, O_3, NO_2, SO_2 and larger hydrocarbons. Now it is a widely used technique in environmental remediation or treatment of pollutants. Even though measurements of Hydroxyl radical have proven to be very difficult, because hydroxyl radical has a very short in vivo half-life of approximately 10^{-9} seconds and a high reactivity, but the detection of hydroxyl radical is not a trivial process. Although there are various techniques reported for the detection of hydroxyl radicals, they all have limitations.

Gas chromatography with stable isotope dilution mass spectrometry (GC/MS) or high-performance liquid chromatography (HPLC) is indirectly used to identify and quantify hydroxyl radical by the interaction of hydroxyl radical with targeting organic reagents. However, most of them involve more complex analytical procedure using expensive solvents or chemicals. Now, one of the most commonly used techniques is the electron spin resonance (ESR) spectrometry measurement. It is based upon the measurement of 2, 3- and 2, 5-dihydroxybenzoic acid isomers formed when reactive oxygen species react with salicylic acid. However, the ESR measurement is also having certain difficulties including tediousness, cost and stability. In addition, hydroxyl radical and superoxide anion cannot be separately detected by ESR in a sample under some conditions.

Thus, in this paper, our objective was to evaluate a hydroxyl radical detection technique that could overcome some of the challenges described in the preceding paragraph. At the same time looking forward to quickly identify hydroxyl radical from the active oxygen species, and can quickly measure the hydroxyl radical relative density。Figure 6-3 shows schematic diagram of the hydroxyl radical instrument developed and chemiluminescent measurement of hydroxyl radical identifying and concentrations in this study. Here, chemiluminescent measurement was chosen, and single-tube type luminometer with multi-color assay detection system could be used as a semi-quantitative and qualitative tool.

Luminescence method used the luminous agents of luminol, MCLA and MPEC and so on. Then we captured the light from the reaction of luminescent reagents and active oxygen species. The figure 6-4 showed us that the light phenomenon of the reaction between luminol and hydroxyl radical. Chemiluminescence method is simply said, it was that chemical reaction made the material became excited state at first. Then the light was produced when the excited state reverted to the basal state. Mentioned reactions were based on chemical oxidation reactions in here. When some active oxygen species which had the characteristics of emitting light were detected, we needed to choose the target luminous agent, which could highly reacted with detected active oxygen species. In addition, we also needed to add corresponding antioxidant into the target active oxygen species to capture the target reactive oxygen species. At last, according to the degree of light resistance of antioxidant, we could measure oxidation inhibitor values. Antioxidants were also chosen according to different kinds of target active oxygen species. In this experiment, through changing the amount of light, and the selection of corresponding luminescent reagent and antioxidant, we could distinguish hydroxyl radical from the target sample of active oxygen species.

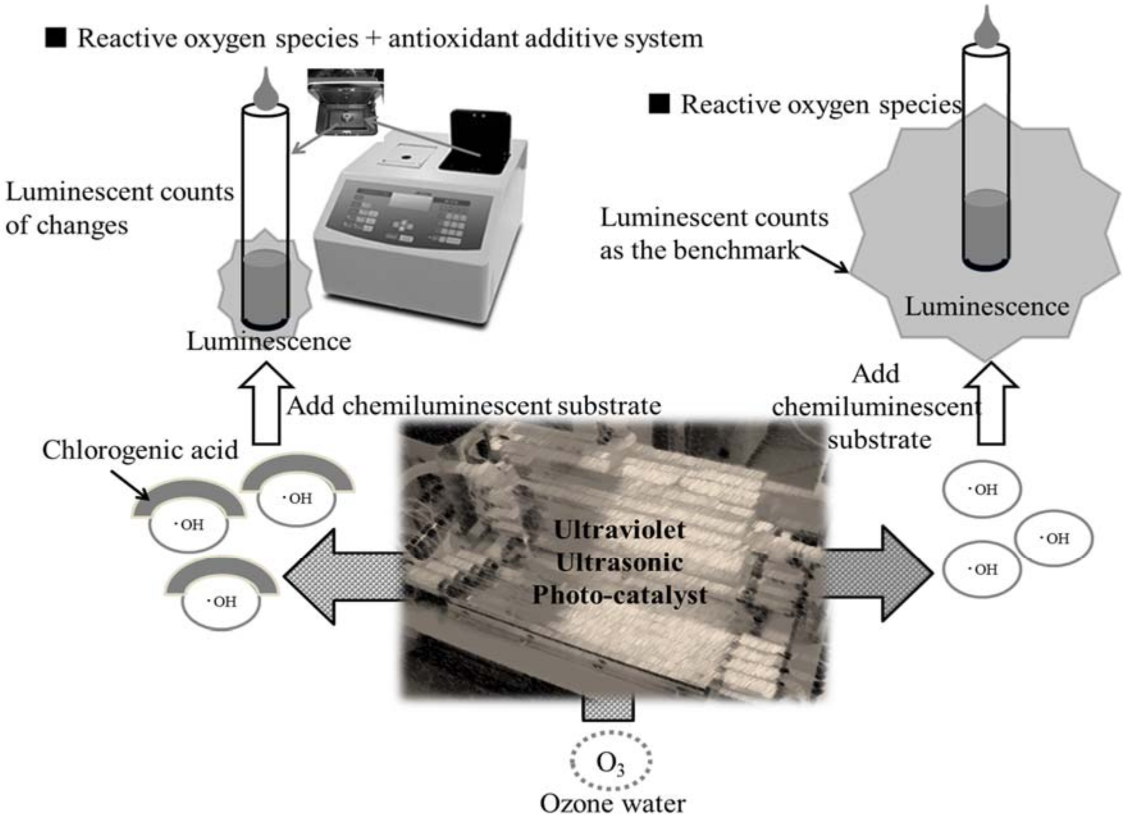


Figure 6-3 Schematic diagram of the hydroxyl radical instrument developed and chemiluminescent measurement of hydroxyl radical identifying and concentrations

Figure 6-4 Light emission from the reaction between luminol and hydroxyl radical

In addition, in order to largely promote hydroxyl radical generating efficiency in this study, the technology is developed which comprehensively uses ozone, ultraviolet illuminating, 300 kilohertz ultrasonic and titania nanotube photocatalyst loaded site-selectively with metal oxide nanoparticles, meanwhile adopts the method of high velocity impact of forging thermal spraying, thereby forming on the surface of fused quartz titanium dioxide photocatalyst thin-film coating of high activeness and compactness. Experiments show that this technology can produce hydroxyl radical water efficiently, and that have a conspicuous effectiveness on environmental remediation and treatment of pollutants.

6.5.1.1 AB-2270 Luminescencer Octa

Chemiluminescence measurement has become extremely popular in recent years. It is often used to determine the amount of a specific unknown or targeted material in the sample of interest, and chemiluminescence is the light emitted by a chemical reaction. Measurement of chemiluminescence from a chemical reaction is essential and highly useful because the concentration of an unknown material can be inferred from the rate at which luminescence is emitted. The rate of luminescence output is directly related to the amount of luminescence emitted, and proportional to the concentration of the known luminescent material.

AB-2270 Luminescencer Octa is a personal single-tube type luminometer with built-in a multicolor assay detection system. The analytical technique of AB-2270 Luminescencer Octa used to measure chemiluminescent reactions, has several advantages over other analytical techniques for hydroxyl radical detection. Extraordinary high-sensitivity; a wide dynamic range; inexpensive instrumentation; easy operation with user-friendly menu driven software; and applicable to various reactive oxygen species separation of analysis with multiple chemiluminscence reagents and various types of antioxidants, including flush and glow reaction, or single and dual assay application. Meanwhile, AB-2270 Luminescencer Octa is capable of separating and multiple luminescence signals simultaneously using its original colour separation mechanism. Colour separation requires optic filters, and is carried out using one filter than the number of luminescence signals.

6.5.1.2 Antioxidant

An antioxidant is a molecule that inhibits the oxidation of other molecules. Oxidation is a chemical reaction that transfers electrons or hydrogen from a substance to an oxidizing agent. Oxidation reactions can produce free radicals. In turn, these radicals can start chain reactions. When the chain reaction occurs in a cell, it can cause damage or death to the cell. Antioxidants terminate these chain reactions by removing free radical intermediates, and inhibit other oxidation reactions. They do this by being oxidized themselves, so antioxidants are often reducing agents such as thiols, ascorbic acid, or polyphenols. Substituted phenols and derivatives of phenylenediamine are common antioxidants used to inhibit gum formation in gasoline. Although oxidation reactions are crucial for life, they can also be damaging; plants and animals maintain complex systems of multiple types of antioxidants, such as glutathione, vitamin C, vitamin A, and vitamin E as well as enzymes such as catalase, superoxide dismutase and various peroxidases. Insufficient levels of antioxidants, or inhibition of the antioxidant enzymes, cause oxidative stress and may damage or kill cells. Oxidative stress is damage to cell structure and cell function by overly reactive oxygen-containing molecules and chronic excessive inflammation. Oxidative stress seems to play a significant role in many human diseases, including cancers. The use of antioxidants in pharmacology is intensively studied, particularly as treatments for stroke and neurodegenerative diseases. For these reasons, oxidative stress can be considered to be both the cause and the consequence of some diseases. Antioxidants are widely used in dietary supplements and have been investigated for the prevention of diseases such as cancer, coronary heart disease and even altitude sickness. Although initial studies suggested that antioxidant supplements might promote health, later large clinical trials with a limited number of antioxidants detected no benefit and even suggested that excess supplementation with certain putative antioxidants may be harmful. Antioxidants also have many industrial uses, such as preservatives in food and cosmetics and to prevent the degradation of rubber and gasoline.

6.5.1.3 Chemiluminescence analysis

Chemiluminescence was measured using a chemiluminessensor. One hundred micro liter of the reacted water sample was placed in a measurement tube, 100 μl of luminol solution was added and the chemiluminescence was measured for 10 s. On the other hand, the reacted water sample was reacted with 50 μl of chlorogenic acid solution (35 mg ml^{-1}) before the addition of the luminol solution. Then, the luminol solution was added and the chemiluminescence was measured for 10 s. Figure 6-5 showed us the chemiluminescence analysis principle and steps for superoxide.

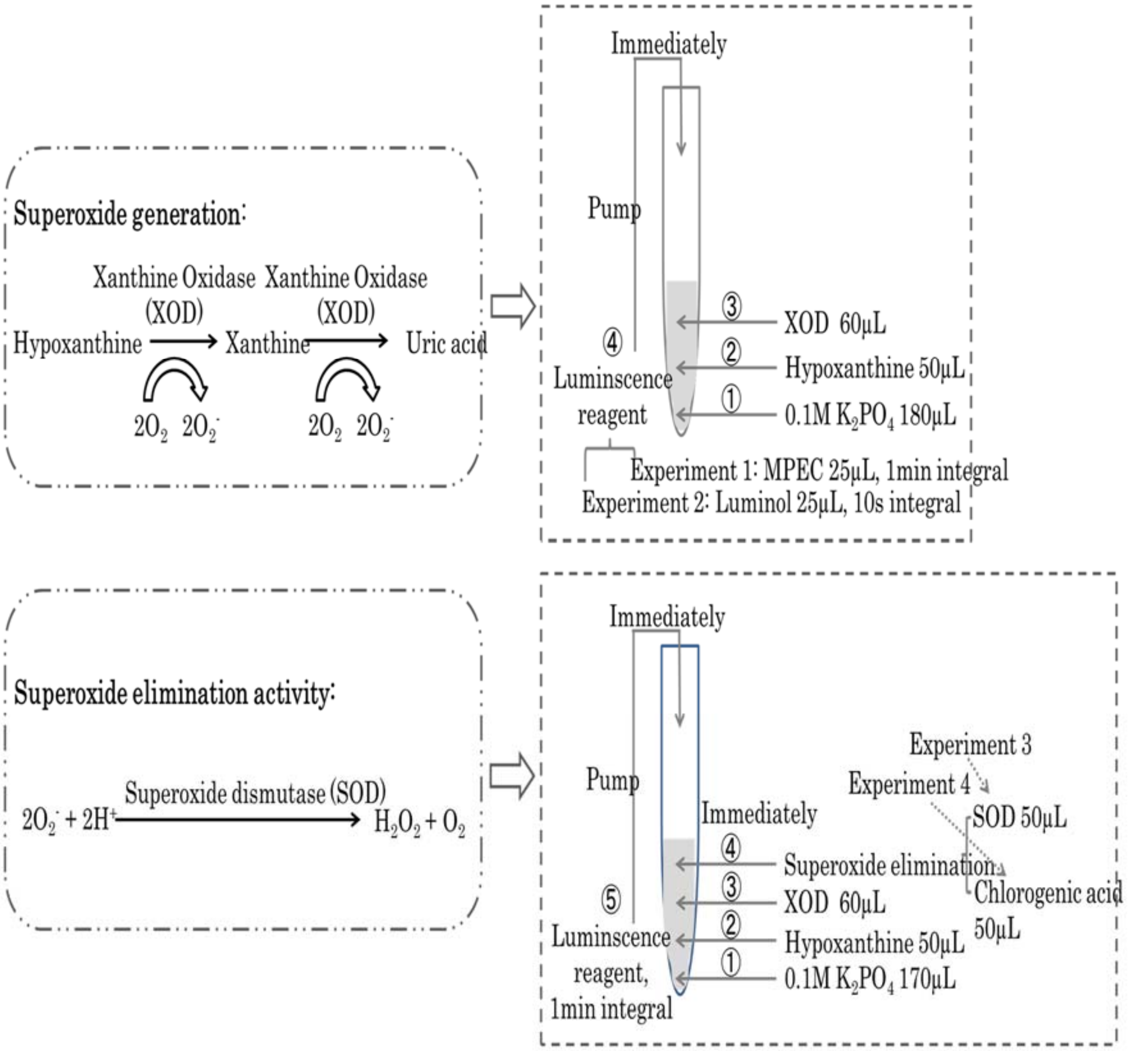


Figure 6-5 Chemiluminescence analysis principle and steps for superoxide

6.5.2 Others

PH, EC, O_3 concentration and ORP were measured using a pH meter (Japanese Society of Water Supply, 2001), an EC meter (Japanese Society of Water Supply, 2001), an O_3 analyzer and an ORP meter, respectively. Oxidizing substances were measured by the titration method with 0.01 N $Na_2S_2O_4$ solution (Japanese Society of Water Supply, 2001) for free I_2. CODMn was measured by the $KMnO_4$ method (Japanese Society of Water Supply, 2001). Metals were measured by the AAS method (Japanese Society of Water Supply, 2001). The radical compounds produced were measured by the GC/MS method (Japanese Society of Water Supply, 2001).

6.6 Results and discussion

6.6.1 Production of active intermediates

Though pH decreased slightly compare to that of the primary O_3 water, it increased slightly with the photocatalyst. Though EC deceased SSW > UVR > SSW + UVR in turn, it increased to the value of the primary O_3 water with the photocatalyst. Those results show that the photocatalyst produces large amount of EC and small amount of acid substances. Though oxidizing substances decreased SSW + UVR > UVR in turn, they increased with the photocatalyst.

The composition of the oxidizing substances was also investigated. Though O_3 deceased by SSW irradiation, over half of the oxidizing substances was those except for O_3 with the photocatalyst. By UVR irradiation, O_3 was not detected and small amount of the other oxidizing substances were detected. By SSW and UVR irradiation, O_3 was not detected and the other oxidizing substances increased. With the photocatalyst, they further increased.

Hydrogen and OH radical are produced from water at 185 nm of UVR irradiation as the photochemical reaction 4. Though those radicals are not produced at 254 nm, OH radical is produced as the reaction 5 if H_2O_2 was produced.

$$H_2O \rightarrow \cdot H + \cdot OH \qquad (4)$$

$$2H_2O_2 \rightarrow OH^- + \cdot OH + HO_2^- + H^+ \qquad (5)$$

This TiO_2 photocatalyst is that of nano-reaction field separation type and an oxidation part and a reduction part are separated. Two electron oxidation occurs in the hole of the photocatalyst as the reaction 6 and H_2O_2 is produced from water.

$$2H_2O + 2h^+ \rightarrow H_2O_2 + 2H^+ \qquad (6)$$

If dissolve O_2 exists in water, O_2 receives an electron and $\cdot O_2^-$ is produced as the reaction 7. Further, H_2O_2 is produced as the reaction 8 and is converted to OH radical as the reaction 9.

$$O_2 + e^- \rightarrow \cdot O_2^- \qquad (7)$$

$$\cdot O_2^- + 2H^+ + e^- \rightarrow H_2O_2 \qquad (8)$$

$$H_2O_2 + e^- \rightarrow \cdot OH \qquad (9)$$

By SSW irradiation, H and OH radical are also produced by the thermal decomposition of H_2O as the reaction 10. If dissolve O_2 exists in water, O radical is also produced as the reaction 10.

$$O_2 \rightarrow 2O \cdot \qquad (10)$$

Ozone is converted to H_2O_2 at 254 nm of UVR irradiation as the reaction 11 and OH radical is produced as the reaction 12.

$$O_3 + H_2O \rightarrow O_2 + H_2O_2 \qquad (11)$$

$$H_2O_2 \rightarrow 2 \cdot OH \qquad (12)$$

The active intermediates produced by the SSW and UVR (photocatalyst) irradiation of O_3 water are considered from these reactions. It was considered that some radicals were contained in the other oxidizing substances.

6.6.2 Behaviors of active intermediates

Figure 6-6 shows the changes of ORP. The water containing O_3 showed high ORP after 1 h. On the other hand, the water containing oxidizing substances except for O_3 showed low ORP because of small amount and short lifetime. However, the oxidizing substances exist for 5 min in case of SSW + UVR irradiation. The oxidizing substances except for O_3 are very easy to decompose (like a radical) because those ORP were very low in spite that about 1/3 of the oxidizing substances to the primary O_3 water existed. If the produced radicals part from the reactor, they can exist in the nano or micro bubble generated by SSW irradiation.

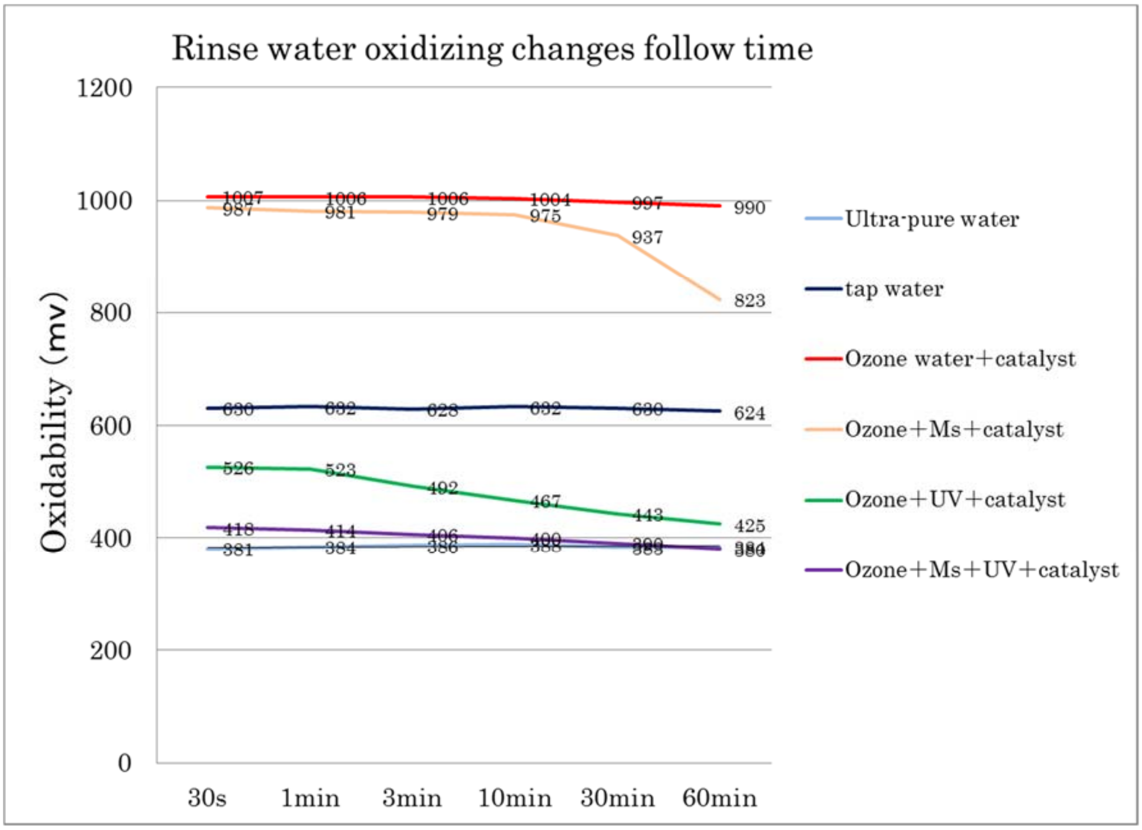


Figure 6-6 OPR change of generated oxidizing substances with time

6.6.3 Identification of hydroxyl radical

6.6.3.1 Reaction with metals

Change the experiment conditions, and then observe the influences ultraviolet, ultrasonic, and titania nanotube photocatalyst have on hydroxyl radical generation, ascertaining the optimal generating environment for hydroxyl radical. Finally, confirm the metals ionization effect. Contemporarily, in Japan, ozone water is most frequently adopted as a cleaner in the process of semiconductor precision products cleaning. And several research studies have been published on cleaning processes that combine ozone with HF. So, ozone water has been found useful in removing the metal impurities, such as copper and iron, on wafer surface, although not to the same extent as other chemistries such as HF. However, for metal impurities such as zinc, nickel, silver and other metals, which deposit on the wafer surface as metal hydroxides or metal oxides, it is not effective when used alone. Therefore, we expect that hydroxyl radical can have the ability of metal removal and particle removal, because hydroxyl radical reaction is fast and non-selective. But before comparing metal impurities cleaning effects between ozone and hydroxyl radical, we must fully grasp the dynamic state of the metal ionization, because the metal impurities or the oxide may be dissolved into high-purity water using hydroxyl radical, enabling metal removal.

We selected several common and typical metal impurities (powders of Zn, Al, Fe, Ni, Cu and Ag). Put the 0.3 g metal impurities into 20ml Teflon bottles respectively, after all Teflon bottles were precleaned with the solution (H_2SO_4:H_2O_2=4:1, 10 min, RT) to remove the organic contaminants. In many cases, hydroxyl radical must act directly on a surface, since hydroxyl radical that are generated too far away from the surface become deactivated and lost. In this paper, we make 20ml hydroxyl radical water that is generated by hydroxyl radical generation system using 6.5 ppm ozone water instantly flow into the bottle, and keep water transmission distance almost zero. And then, keep reacting hydroxyl radical water and 6.5 ppm ozone water respectively with 0.3 g metal impurities for 2 days to make the part of metal impurities dissolve into water. After 2 days, filter out the metal powders, and then measure the concentration of the metal ion in the residual liquid with atomic absorption spectrophotometer. After analyzing the measured results we can verify hydroxyl radical’s metal ionization degree. In the experiment above, hydroxyl radical water is produced by illuminating ozone water of 6.5 ppm with ultraviolet and 1 MHz ultrasonic in the hydroxyl radical generating equipment.

Figure 6-7 shows the concentrations of metal ions after 2 days reaction with the reacted water sample. These ionization tendencies are Zn > Fe > Ni > Cu > Ag in turn. The concentration of Fe ion, which is easy to ionize, in the primary O_3 water was the highest. However, the concentrations of Ni, Cu or Ag ion, which are difficult to ionize, in the solution of oxidizing substances except for O_3 are higher than in the primary O_3 water. This shows that the oxidizing powers of these oxidizing substances (like a radical) are stronger than O_3. Further, Zn ion, which is very easy to ionize, was hardly detected in the primary O_3 water but a high concentration of Zn ion was detected in case of SSW + UVR irradiation. This shows that the surface of Zn powder was converted to ZnO, which is hardly soluble in water, with O_3. In case of SSW + UVR irradiation, it was considered that OH reacted with Zn and water soluble Zn-OH compound was produced. Zn and Al impurities are the examples. Like zinc, it is difficult to dissolve in water, when zinc reacts with ozone water. From figure 6-8, we can find that ozone can make Zn ionization when the reaction time is short (10s). But when we greatly increase reaction time between ozone and Zn (2 days), the concentration of zinc ion is zero in solution. We speculate that the Zn ion is further oxidized into the oxide and hydroxide by ozone. And they are difficult to dissolve in water. However, hydroxyl radical water can make zinc oxide and zinc hydroxide on the surface further oxidized, forming metal complex that can easily dissolve in water, so as to reach the purpose of removing metal impurities and improving clean efficiency. For the metal ionization effect and mechanism of hydroxyl radical, it was revealed by many research papers. Other metals such Fe, Ag and Ni, hydroxyl radical water can make them better dissolve into water, because hydroxyl radical oxidation ability is far stronger than ozone. In the future, it is expected that hydroxyl radical can remove and decompose the organic contaminant that are difficult to be removed by ozone and chlorine.

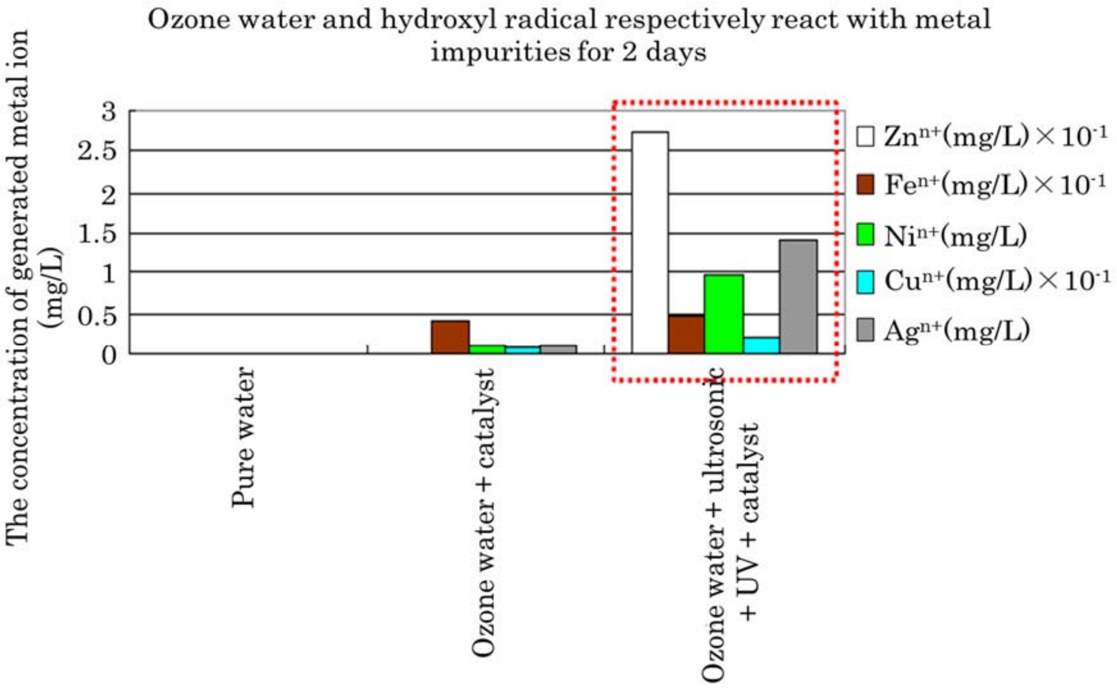


Figure 6-7 Concentration of metal ions after 2 days reaction with the reacted water sample

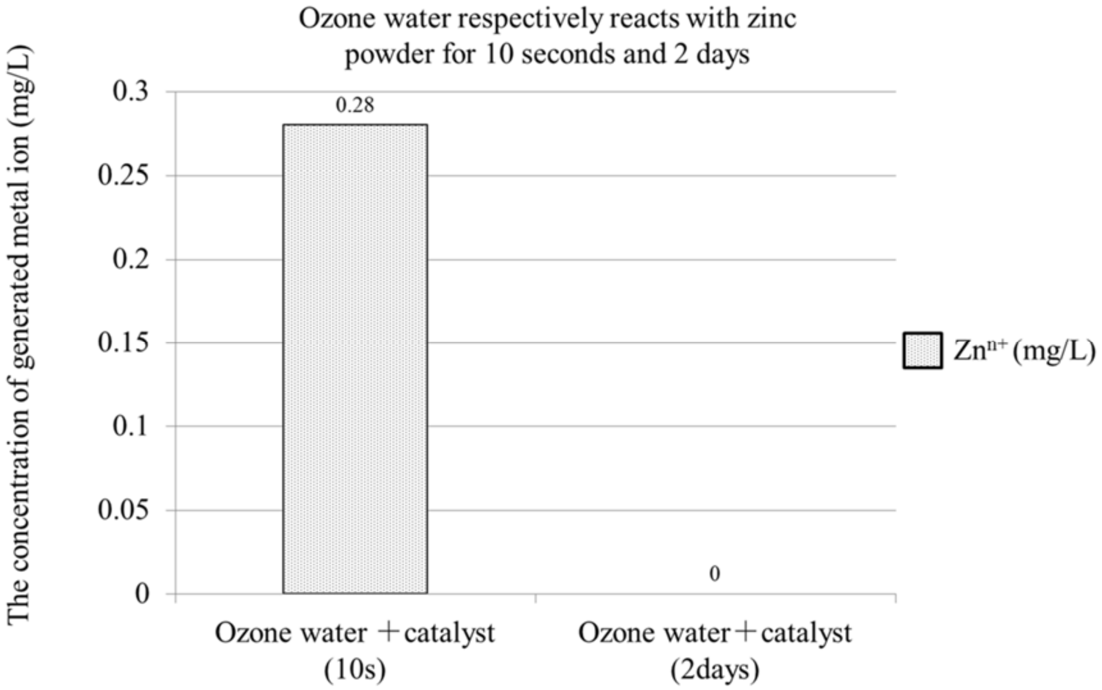


Figure 6-8 Change of the concentration of generated zinc ion by ozone water when the reaction time changing.

6.6.3.2 Qualitative analysis of hydroxyl radicals by chemiluminescence measurement

The chemiluminescene method with luminol and chlorogenic acid was performed for the oxidizing substances except for O_3. The chemiluminescene, which shows a radical, was observed when the solution was reacted with luminal. The chemiluminescene was not observed when the solution was added with chlorogenic acid before the addition of luminal. As chlorogenic acid reacts with hydroxyl radical and interferes the chemiluminescene between hydroxyl radical and luminal, it was considered that most of the oxidizing substances consisted of hydroxyl radical.

Analyze the species of the oxidant generated with Luminescencer Octa AB-2270. When measuring, for the possible reactive oxygen species generated, select out the highly functional drugs that can conduct chemiluminescence reaction with those objective oxidant, and test out the reactive oxygen species with the help of chemiluminescence. In this paper, for capturing hydroxyl radical, lumino is selected as chemiluminescence reagent. Then select out the antioxidant in accordance with hydroxyl radical, here we use chlorogenic acid as the antioxidant. At last, evaluate the luminescence on the basis of chemiluminescence reagent and antioxidant. Chemiluminescent results are showed in figure 6-9. The increase of Luminescent counts is attributed to the production of hydroxyl radical generated by Fenton's system, because chemiluminescence is the light emitted by a chemical reaction between hydroxyl radical and lumino. And when adding chlorogenic acid, with the increase of addition amount, the rate of luminescence inhibition of hydroxyl radical also increases. But in the experiment, for hydrogen peroxide, the chemiluminescence reaction by lumino alone can't be happened, it also need to add horse radish peroxidase into lumino to be Luminol-HRP. Luminol-HRP can react with hydrogen peroxide to produce chemiluminescence. In addition, other reactive oxygen species such as superoxide and singlet oxygen, lumino can react with them to produce chemiluminescence. But, when adding chlorogenic acid, chemiluminescence inhibition is not happened, actually luminescent counts increase. For superoxide, if we want to inhibit chemiluminescence, we need to add superoxide dismutase (SOD) as the antioxidant. It is shown as figure 6-10. In other words, hydroxyl radical can be accurately and quickly detected by luminescencer octa AB-2270 using specifical chemiluminescence agent and antioxidant from the sample of interest. The chemiluminescence method is highly selective and sensitive to detect reactive oxygen species. We can conclude that the radical generated by our experiment device is hydroxyl radical by capturing chemiluminescence reaction and the change of relative volume of luminescence, and we can indirectly measure hydroxyl radical concentration by the previous method in the section of experimental setup.

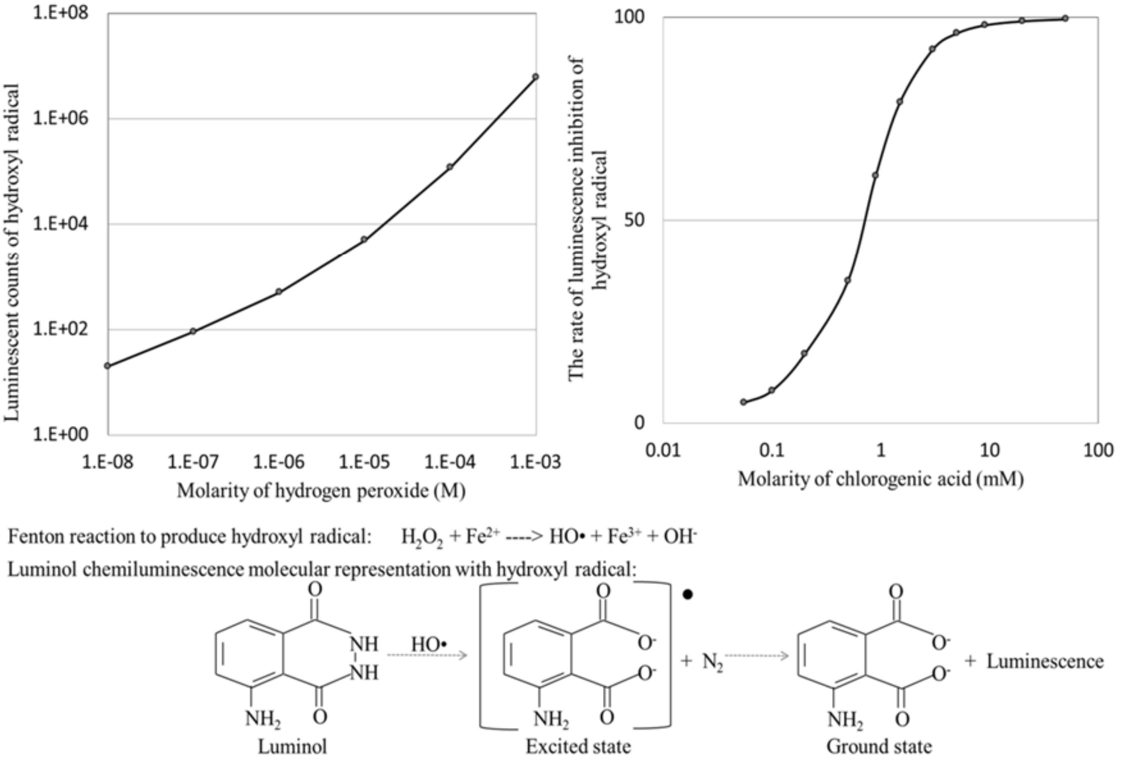


Figure 6-9 Detection of hydroxyl radical using chemiluminescence and the radical-scavenging activity using chlorogenic acid.

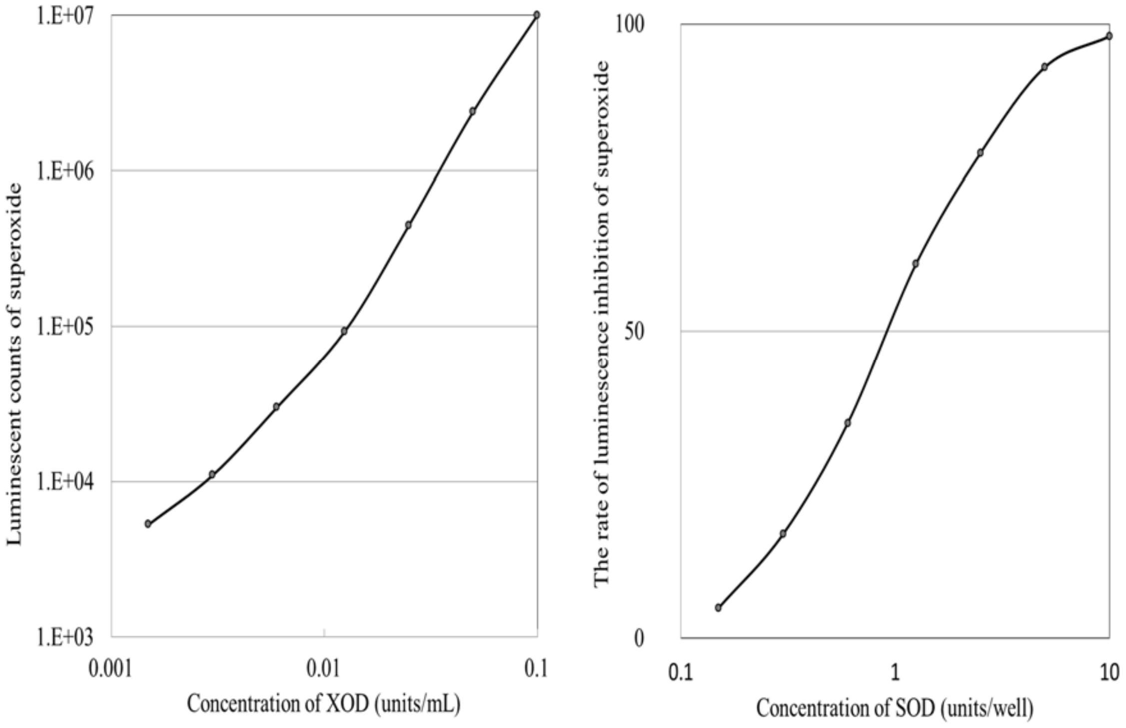
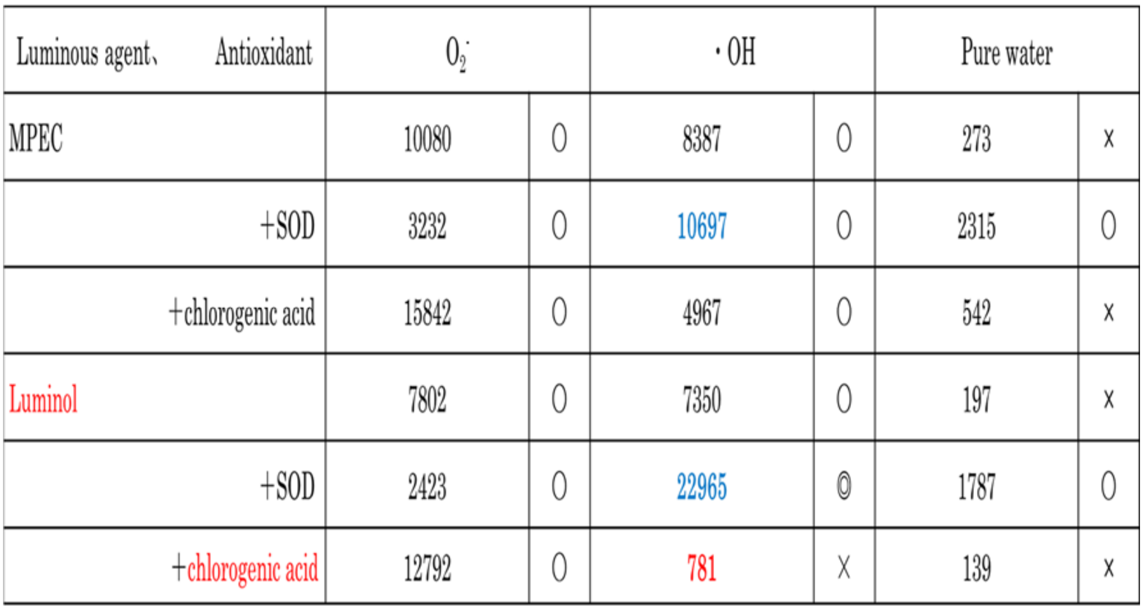


Figure 6-10 Detection of superoxide using chemiluminescence and the radical-scavenging activity using SOD.

For the oxygen free radical agent, MPEC luminescent reagent can cause oxygen radical luminescence, when add chlorogenic acid as elimination reagent, the amount of luminescence is not reduced, it is increased; for the hydroxyl radical, luminol luminescent reagent can lead to hydroxyl radical luminescence, when add chlorogenic acid, the amount of luminescence is drastically reduced, and even lead to luminescence elimination. For generated rinse reactive free radical water, the component of reactive free radical may be oxygen radical, may also be hydroxyl radical. When add luminol as luminescent reagent, the free radical can be caused luminescence by luminescence octa monitor, when add chlorogenic acid as elimination reagent, the amount of luminescence would be drastically reduced, even lead to luminescence elimination, so we can inferred that reactive free radical is hydroxyl radical. The amount of luminescence is shown as table 6-1. From figure 6-11, we can found that the main ingredients of generated rinse water were hydroxyl radical from our device. Because the amount of luminescence got zero after we added the chlorogenic acid into samples. But for the ozone-ultrasonic sample, light is still.

Table 6-1 Luminescent count of free radical reagents under different conditions



Luminous agent、 Antioxidant	O_2^-		·OH		Pure water	
MPEC	10080	○	8387	○	273	x
+SOD	3232	○	10697	○	2315	○
+chlorogenic acid	15842	○	4967	○	542	x
Luminol	7802	○	7350	○	197	x
+SOD	2423	○	22965	◎	1787	○
+chlorogenic acid	12792	○	781	X	139	x

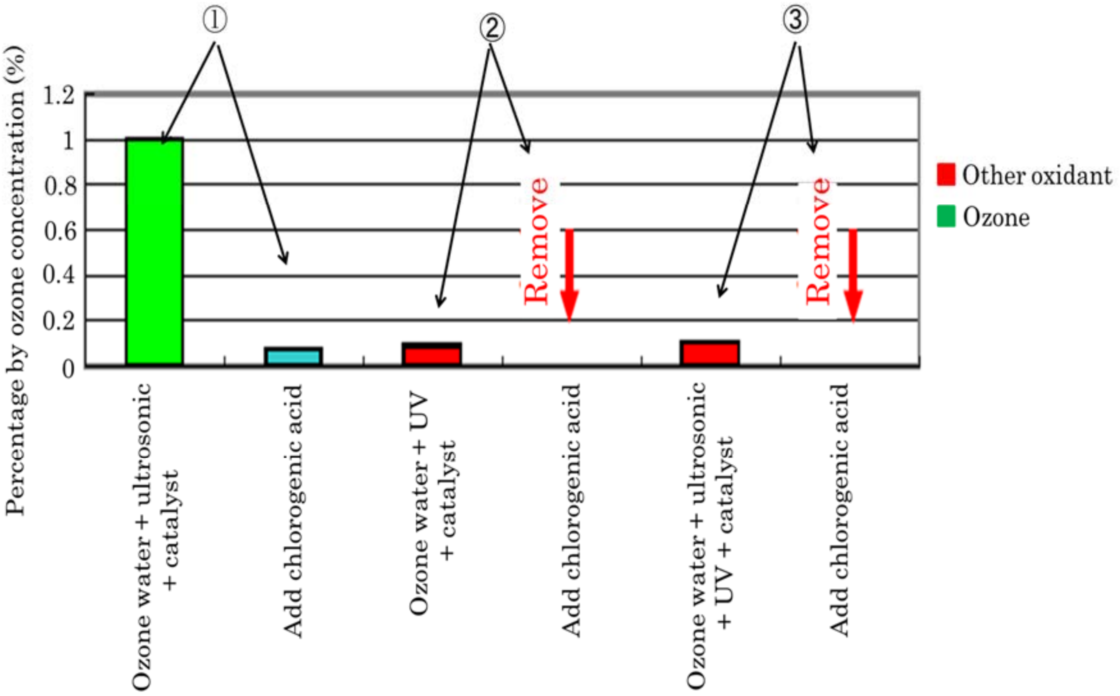
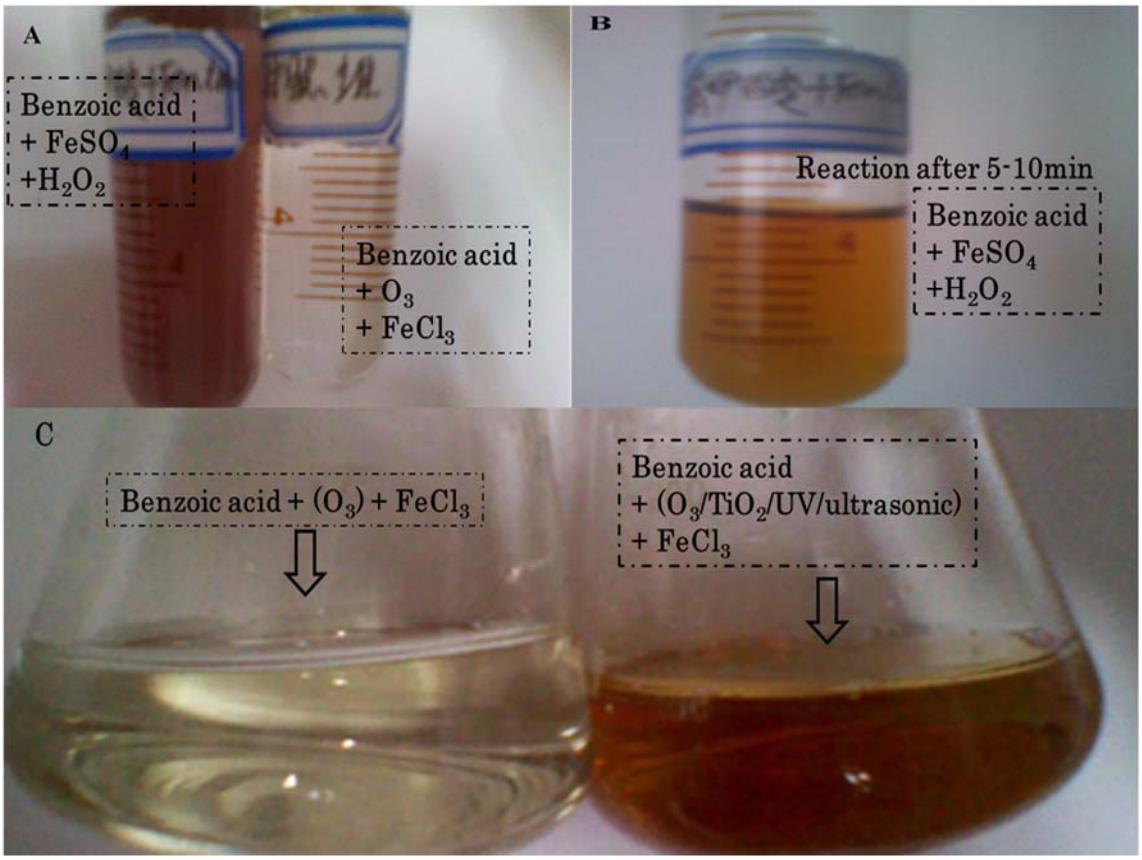


Figure 6-11 Luminescent count change of generated free radicals under different conditions by the mobile free radical rinse water equipment



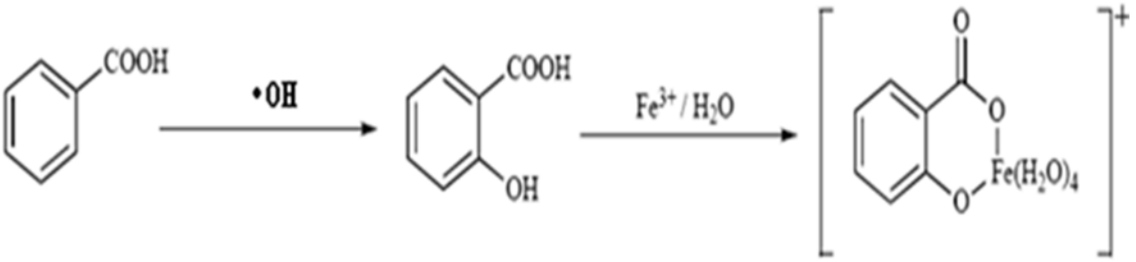


Figure 6-12 Chromogenic reaction between hydroxyl radical and benzoic acid in the ferric iron environment

At first, we generated hydroxyl radical by Fenton's reaction, we can find chromogenic reaction between hydroxyl radical and benzoic acid in the ferric iron environment. But ozone con not react with benzoic acid. So the generated rinse water reacts with benzoic acid to generate chromogenic reaction when we add the rinse water into the ferric iron solution. It is shown as figure 6-12. The result says that chemiluminescence analysis is right.

6.6.3.3 Reaction with organic compounds

Though the reacted water sample was reacted with benzene, ethylbenzene, *o*-xylene, *o*-cresol, bromobenzene and pyridine, the reaction products of these compounds with OH radical were not detected. In case of benzophenone, the reaction product with H radical ($H_2O \rightarrow \cdot H + \cdot OH$) was detected. Method A: Step 1: Generate hydroxyl radicals by (O3-water/UV/MS/ TiO2) method, and then keep still. Step 2: Take a certain sample from the step 1 and make reaction between OH radical and benzene compound generate phenol compound, then take phenol compound to measure concentration by GC/MS (figure 6-13). The concentration of generated hydroxyl radicals decrease quickly with time. And hydroxyl radicals are highly reactive and short-lived. It will be one hot point research that how to increase the residual time of radical.

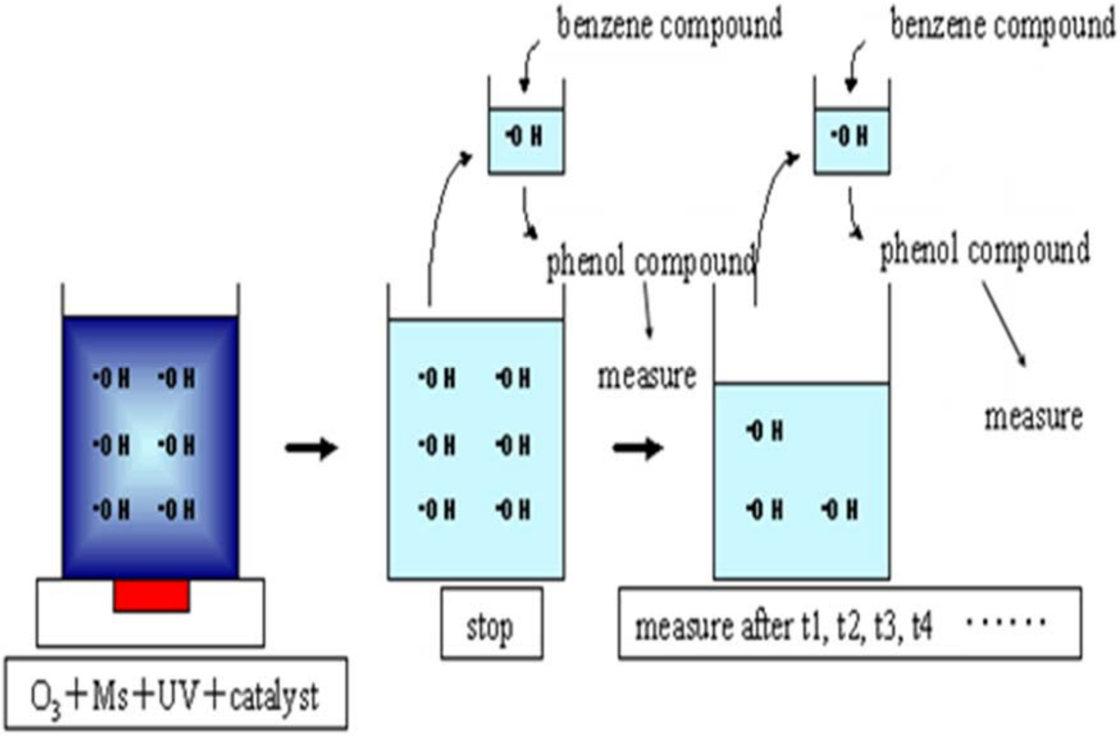


Figure 6-13 Method of measuring the change of generated hydroxyl radical' concentration with time

6.6 Conclusions

The IC wafer washing water was produced by the O_3/UVR/SSW multiple reaction using a low temperature sprayed TiO_2 photocatalyst. The washing water contained mainly OH radical whose oxidizing power is stronger than that of O_3. The produced radicals can exist in nano or micro bubble generated by SSW irradiation if they part from the reactor. The water can wash metals and low molecular weight of organic compounds and can be used as IC wafer washing water. Further, the utilization of the water would expand to the fields of hydrophilic reaction, the prevention of static electricity and the disinfection of foods. In the present study, the detection of hydroxyl radical from different systems (classical and non-classical systems) has been executed by AB-2270 Luminescencer Octa, followed by chemiluminescent measurements with luminol and chlorogenic acid. And chemiluminescent measurement has several advantages over other analytical techniques for hydroxyl radical detection. For example, extraordinary high-sensitivity, inexpensive instrumentation, cost-effective, easy operation with user-friendly menu driven software, speedy and stability. The developed method was not only useful for the detection of hydroxyl radicals in low level concentration, but also helpful to identify the optimal conditions for producing hydroxyl radicals and determination of generated hydroxyl radical count.

But detection of the ambient hydroxyl radical by the chemiluminescent measurement technique can be affected by the ozone interference. In this paper, we report the development of a hydroxyl radical instrument based on the technology comprehensively using ozone, ultraviolet, ultrasonic and high light sensitive titania nanotube photocatalyst. In this technology, the ultraviolet (wavelength is 185 nm, 254 nm, 305 nm and 365 nm) can completely photolyze ozone molecules, meanwhile largely promote hydroxyl radical generating efficiency with the help of ultrasonic and photocatalyst. The ozone interference is negligibly hydroxyl radical in our hydroxyl radical instrument. Moreover, we can combine chemiluminescent measurement with UV spectrophotometry technique to clear up the ozone interference. Overall, the developed method could be used for the detection of hydroxyl radical produced by any system.

Chapter Seven - Contaminants cleaning and decomposition Effects by hydroxyl radical

7.1 Introduction

With the high integration of devices in recent years, cleanliness management has become increasingly important in the field of semiconductor manufacturing. Wafer surface are easily polluted by metal, oily and organic contaminants. In particular, the device characteristics are degraded by metal impurities remaining on the wafer surface, so it has a significant impact on the manufacturing yield of the device. Thereby the processes of protecting semiconductor surface from contaminant and removing the contaminants are indispensable part of semiconductor manufacturing. If the pollutants concentration is low in the chemical cleaning drugs side, the metal impurities on the surface can be removed by gradually dissolving and diffusion as the metal ions. Traditional cleaning technology needs lots of time, energy, chemical cleaning drugs and ultrapure water, and drugs such as hydrogen fluoride and hydrogen peroxide can do harm to human health and cause secondary contaminant. Nowadays, in many developed countries, it is shifting to the cleaning technology that takes into account the environment more from the existing technology that has consumed a large amount of chemical drugs. Ozone water is usually used to clean semiconductor precision products, but for some contaminants that are difficult to be decomposed, the decomposition will not work well. Accordingly, more and more scholars pay attention to hydroxyl radical. Hydroxyl radical have strong abilities to capture electrons, namely oxidizability, and its oxidation potential is 2.8v, and thus is among the best oxidants only after fluorine in nature. Because oxidizing power of hydroxyl radical is far stronger than ozone water, we expect hydroxyl radical is able to improve the cleaning effect of the metal impurities. Besides, it can produce instantaneous chain reaction with most of the organic pollutants, quickly and indiscriminately oxidizing the deleterious pollutants as CO_2, H_2O and mineral salt, without any secondary contaminant. In the field of semiconductor precision products cleaning, hydroxyl radical water is so suitable that it can replace drug cleaners and ozone water, because it has many advantages. For example, it could be used in room temperature. Further, compared with the traditional method, we have confirmed that the cleaning time and the amount of ultrapure water for cleaning were less, when we obtained an equal cleaning effect. The hydroxyl radical can also reduce the cost of water treatment. In other words, when the factory imports the technology of hydroxyl radical, it can be expected to save energy, save resource, efficiently clean and reduce environment burden, etc.

In this paper, in order to improve the cleaning efficiency, meanwhile improve the concentration of hydroxyl radical as high as possible, it is necessary to optimize flow mode for the generation of hydroxyl radical. Through long-range research and constant improvement on methodology, we find that the technology combining ozone, ultraviolet, ultrasonic and photocatalyst is able to produce high-concentration hydroxyl radical. And in a short time the technology uses minimum energy to effectively remove the oily, metal and organic contaminants attached on semiconductor surfaces that are hard to be decomposed. Meanwhile, in this technology, high light sensitive titania nanotube photocatalyst is made into thin-film coating of high activeness and compactness with the method of high velocity impact of forging thermal spraying. In addition, in the process of cleaning, replacing kilohertz ultrasound by low-megahertz (MHz) ultrasonic is able to decrease the damage ultrasonic does to semiconductor precision products when cleaning. The main purpose of the paper shows metal ionization degree and organic contaminants' decomposition of analysis results after hydroxyl radical reacts with metals or organic contaminants. And make it compared with ozone' results. The analysis results laid a foundation for the future wafer cleaning experiment with hydroxyl radical water instead of ozone water.

7.2 Experiment of metals contaminants cleaning and decomposition effects by hydroxyl radical

7.2.1 Materials and methods

The photocatalyst was kindly supplied by Catalysts & Chemicals Ind. Co., Ltd. The photocatalyst was used after calcination at 350 °C for 3 hours in order to improve the crystallinity of the photocatalyst. TiO_2 thin-film coating was generated by using High Velocity Impact Forging thermal spraying technology from FUJIKO Co., Ltd. Ozone water was made from pure oxygen and millipore laboratory water with a laboratory ozonizer (ED-OW-7, EcoDesign, Inc.). Multiple chemiluminescence reagents have been procured from ATTO Corporation for Luminescence-based techniques of reactive oxygen species. Multiple types of antioxidants are made by Wako Pure Chemical Industries, Ltd. Portable ozone monitor was procured from APPLICS Co., Ltd. AB-2270 luminescencer octa was procured from ATTO Corporation for hydroxyl radical detection. The results of metals' ionization were measured by fast sequential atomic absorption spectrometer (VARTAN: AA240FS, Agilent).

7.2.2 Experimental process about verification of the metal ionization

Change the experiment conditions, and then observe the influences ultraviolet, ultrasonic, and titania nanotube photocatalyst have on hydroxyl radical generation, ascertaining the optimal generating environment for hydroxyl radical. Finally, confirm the metals ionization effect. Contemporarily, in Japan, ozone water is most frequently adopted as a cleaner in the process of semiconductor precision products cleaning. And several research studies have been published on cleaning processes that combine ozone with HF. So, ozone water has been found useful in removing the metal impurities, such as copper and iron, on wafer surface, although not to the same extent as other chemistries such as HF. However, for metal impurities such as zinc, nickel, silver and other metals, which deposit on the wafer surface as metal hydroxides or metal oxides, it is not effective when used alone. Therefore, we expect that hydroxyl radical can have the ability of metal removal and particle removal, because hydroxyl radical reaction is fast and non-selective. But before comparing metal impurities cleaning effects between ozone and hydroxyl radical, we must fully grasp the dynamic state of the metal ionization, because the metal impurities or the oxide may be dissolved into high-purity water using hydroxyl radical, enabling metal removal.

We selected several common and typical metal impurities (powders of Zn, Al, Fe, Ni, Cu and Ag). Put the 0.3 g metal impurities into 20ml Teflon bottles respectively, after all Teflon bottles were precleaned with the solution (H_2SO_4:H_2O_2=4:1, 10 min, RT) to remove the organic contaminants. In many cases, hydroxyl radical must act directly on a surface, since hydroxyl radical that are generated too far away from the surface become deactivated and lost. In this paper, we make 20ml hydroxyl radical water that is generated by hydroxyl radical generation system using 6.5 ppm ozone water instantly flow into the bottle, and keep water transmission distance almost zero. And then, keep reacting hydroxyl radical water and 6.5 ppm ozone water respectively with 0.3 g metal impurities for 10 seconds to make the part of metal impurities dissolve into water. After 10 seconds, filter out the metal powders, and then measure the concentration of the metal ion in the residual liquid with atomic absorption spectrophotometer. After analyzing the measured results we can verify hydroxyl radical's metal ionization degree. In the experiment above, hydroxyl radical water is produced by illuminating ozone water of 6.5 ppm with ultraviolet and 1 MHz ultrasonic in the hydroxyl radical generating equipment.

7.2.3 Verify hydroxyl radical's metal ionization degree

After ascertaining the optimal generating environment for hydroxyl radical, we conduct metal ionization degree experiment. The experiment condition is a simulation of wash process with water flow system, and each set of clean liquid will react with the metal impurities for 10 seconds. Results are showed in figure 7-1. It is shown that hydroxyl radical water has far more conspicuous metal ionization effects than ozone water. Compare with ozone water independently, with the new methodology, Zn's ionization rate increased by 5 times, Al's by 2.9 times, Fe's by 3.5 times, Ni's by 2 times, Cu's by 1.3 times and Ag's by 8 times. In the experiment, the concentration of hydroxyl radical is only one-third of ozone's concentration. So, if we use the same concentration between hydroxyl radical and ozone, for the metal ionization effect of hydroxyl radical may be 3 times than now. Although ozone water is not omnipotent for dealing with all of metal impurities, from the experiment results, we can see that ozone water is effective to a certain extent when facing heavy metal like Cu. For Cu, using ozone water to react, which is highly capable of capturing electrons (namely strong oxidization ability), will capture the electrons of Cu, changing them to cation so as to be dissolved by water and easily removed. But strictly speaking, the metal ionization degree of ozone water will be heavily reduced when some oxide and hydroxide that are difficult to react with ozone water form on the metal impurities surface due to natural oxidization. Zn and Al impurities are the examples. Like zinc, it is difficult to dissolve in water, when zinc reacts with ozone water. From figure 7-2, we can find that ozone can make Zn ionization when the reaction time is short (10s). But when we greatly increase reaction time between ozone and Zn (2 days), the concentration of zinc ion is zero in solution. We speculate that the Zn ion is further oxidized into the oxide and hydroxide by ozone. And they are difficult to dissolve in water. However, hydroxyl radical water can make zinc oxide and zinc hydroxide on the surface further oxidized, forming metal complex that can easily dissolve in water, so as to reach the purpose of removing metal impurities and improving clean efficiency. For the metal ionization effect and mechanism of hydroxyl radical, it was revealed by many research papers. Other metals such Fe, Ag and Ni, hydroxyl radical water can make them better dissolve into water, because hydroxyl radical oxidation ability is far stronger than ozone. In the future, it is expected that hydroxyl radical can remove and decompose the organic contaminant that are difficult to be removed by ozone and chlorine.

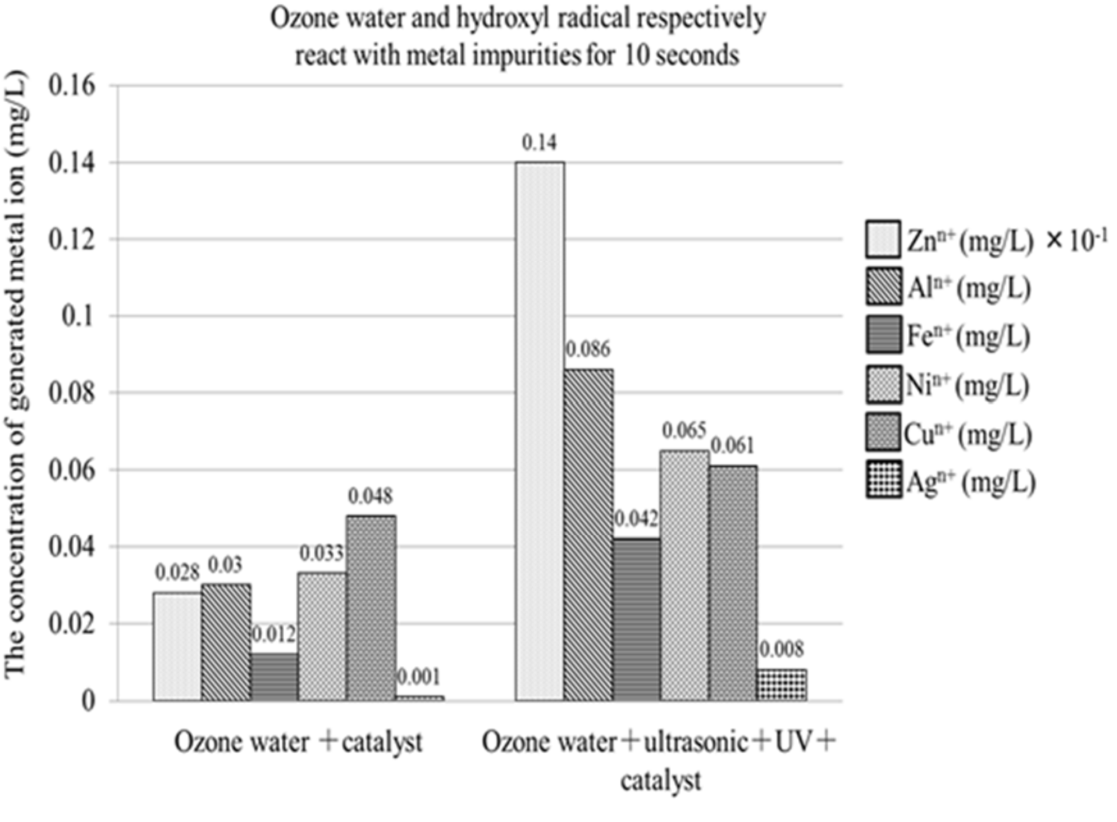


Figure 7-1 Compare metal ionization degree between ozone water and hydroxyl radical water

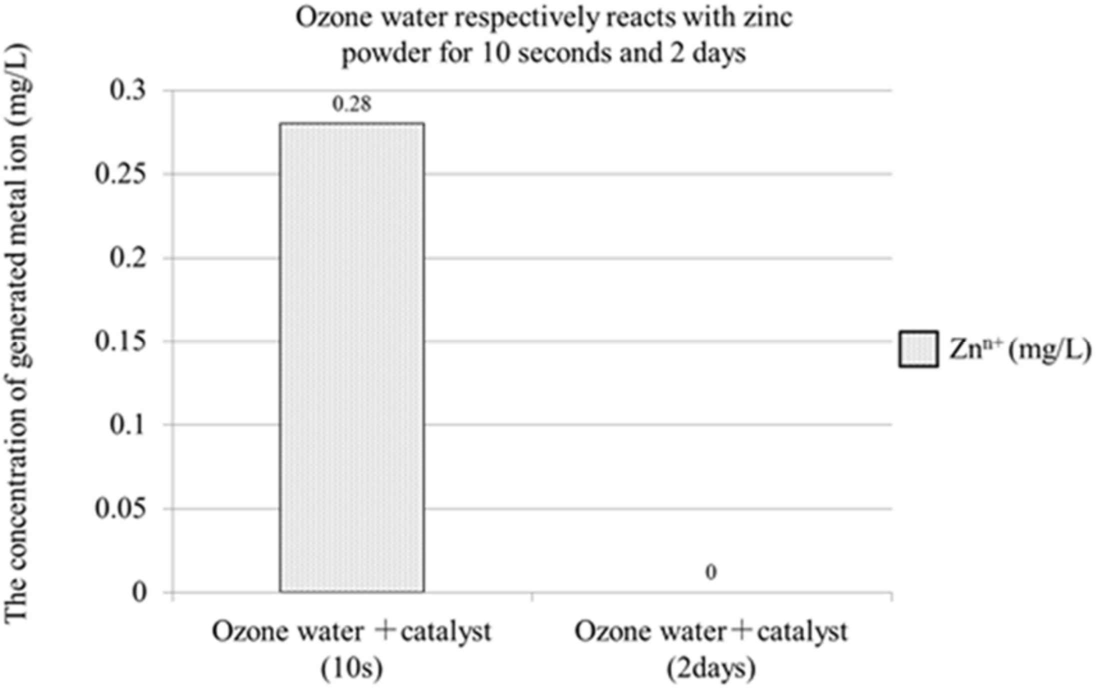


Figure 7-2 Change of the concentration of generated zinc ion by ozone water when the reaction time changing

From figure 7-3, it can be seen that for general metal impurities like Cu, Zn and activity stability of metal impurities like Ag, the metal ionization effects of hydroxyl radical water on them will increase with the concentration of hydroxyl radical water. This is particularly true for Ag. In the hydroxyl radical's cleaning process, when the concentration of hydroxyl radical is low, part of the metal impurities will be ionized, dissolved by water and removed, but due to oxidization, most of them will form as metal oxide and metal hydroxide that are difficult to be dissolved by water. When the concentration of hydroxyl radical is higher, instead of metal oxidation film, the remaining hydroxyl radical can further react with those metal oxide and metal hydroxide, forming metal complex, which is easily dissolved by water, so as to remove the metal impurities. In addition, the metal complex produced by the reaction of metal and targeted liquid is an indirect verification of the generation of hydroxyl radical. The peculiar features of hydroxyl radical showed in dealing with contaminant present its optimistic application prospect.

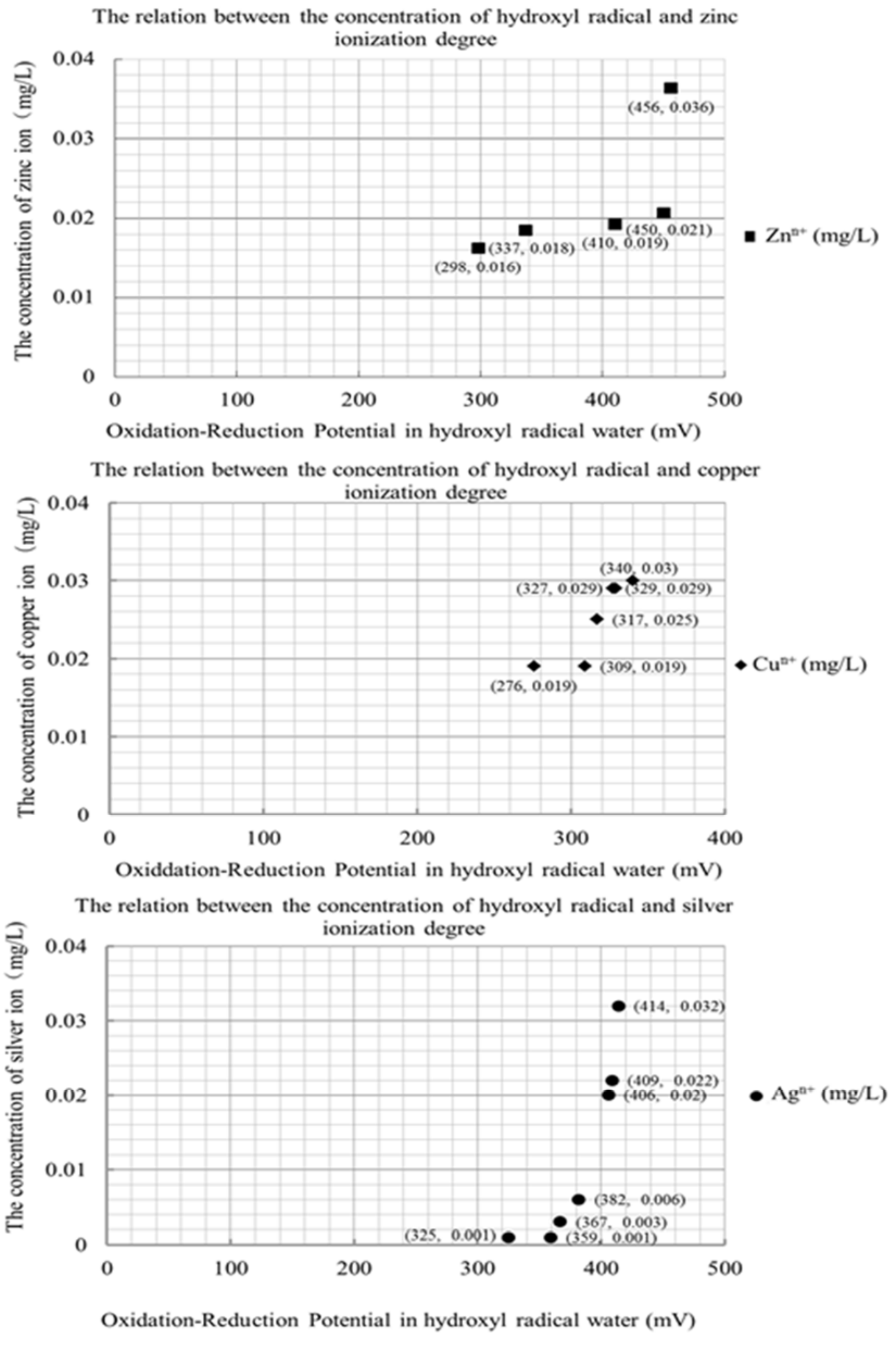


Figure 7-3 Metal ionization degree on Zn, Cu and Ag will increase with the increase of the concentration of hydroxyl radical

7.3 Experiment of organic contaminants cleaning and decomposition effects by hydroxyl radical

7.3.1 Materials and methods

In this research, the reaction between organic contaminants (Dimethyl sulfoxide was purchased from Wako Pure Chemical Industries, Ltd. DL-Tartaric acid was purchased from Nacalai Tesque. Soluble starch was purchased from Wako Pure Chemical Industries, Ltd. Dioctyl phthalate was purchased from Tokyo Chemical Industry Co., Ltd. Dibutyl phthalate was purchased from Tokyo Chemical Industry Co.) and OH radical water are researched. Then the identification results of products of decomposition were measured using gas chromatography-mass spectral (GC-MS). All other chemicals used for mineral salts media and extractions were of analytical grade. The solutions were prepared using deionized water from MiliQ system.

The volume of 1 μL standard and sample solution was injected in GC injection port. The temperature of injection port was maintained at 230 °C, split ratio 1:15, with nitrogen as a carrier gas. The pressure of 14 kpa with flow of 3.2 mL/min was maintained. The temperature of the detector was set at 250 °C. Temperature was maintained at 40 °C for five min and then increased at a rate of 10 °C/min to 55 °C/min and maintained for 5min, finally increased at the rate of 10 °C/min to reach the final temperature of 200 ° C and maintained for 5 min.

In the experiment, hydroxyl radical water is produced by illuminating ozone water of 6.5 ppm with ultraviolet and 1 MHz ultrasonic in the hydroxyl radical generating equipment.

7.3.2 Verify the organic contaminants decomposition effect

Dimethyl sulfoxide (DMSO) is an organosulfur compound with the formula $(CH_3)_2SO$. This colorless liquid is an important polar aprotic solvent that dissolves both polar and nonpolar compounds and is miscible in a wide range of organic solvents as well as water. Figure 7-4 is on the residual ratio of DMSO after the reaction of ozone and hydroxyl radical with DMSO. We can find that dissolved ozone and hydroxyl radical can react with DMSO, but the decomposition effect is not well, because the concentration of ozone. Meanwhile, compare with ozone water, hydroxyl radical can substantially enhance the decomposition of DMSO.

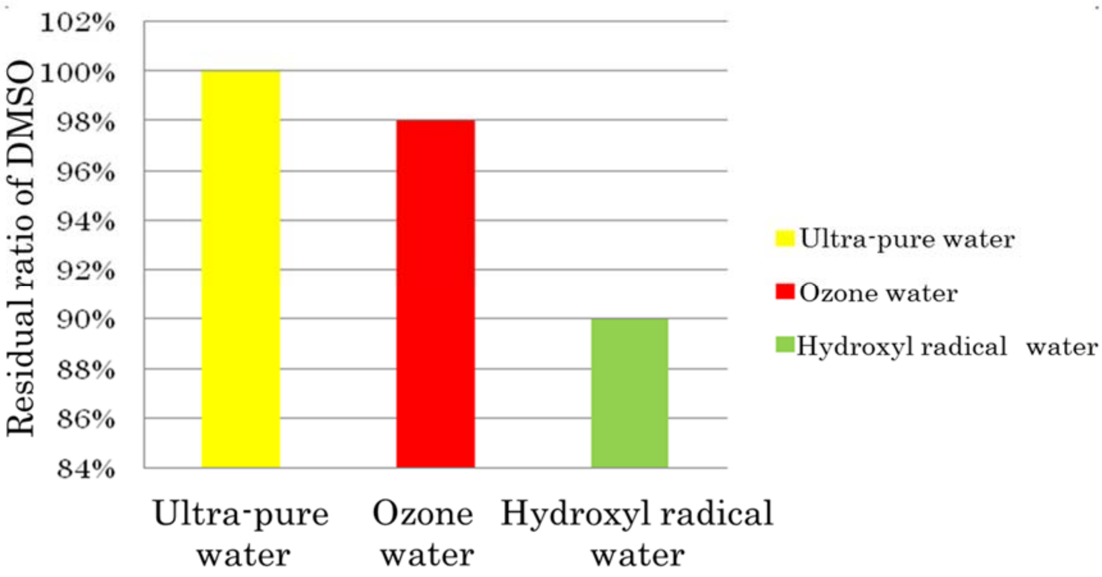


Figure 7-4 Residual ratio of DMSO after the reaction of ozone and hydroxyl radical with DMSO

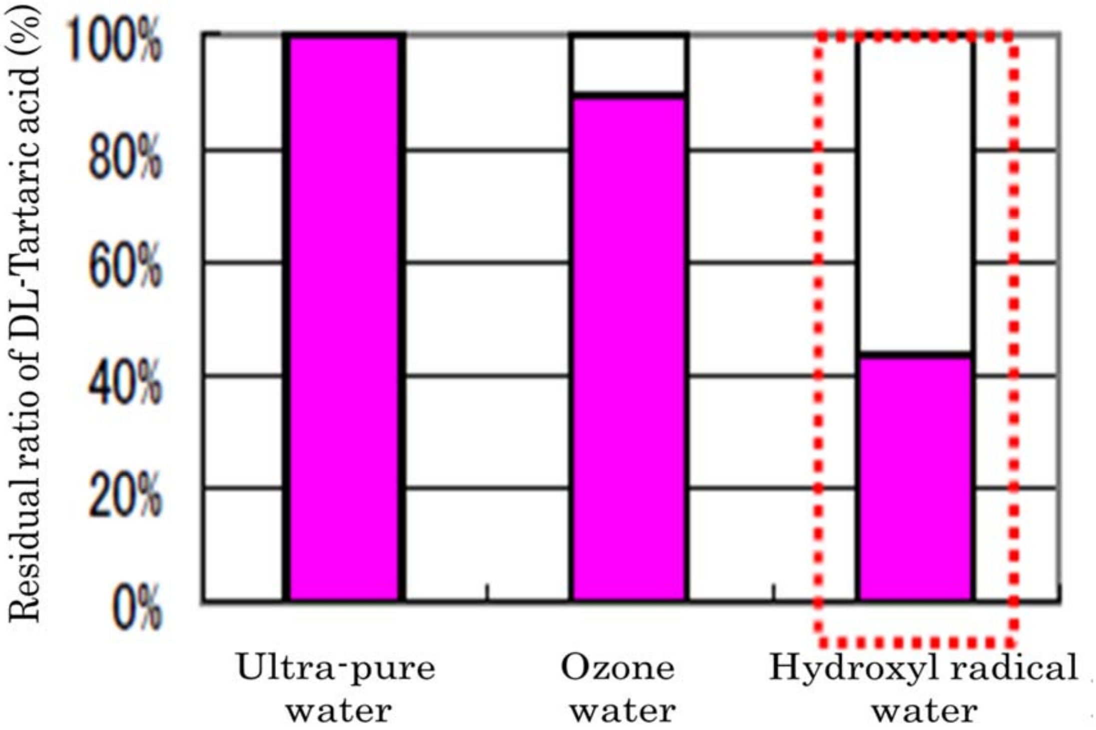


Figure 7-5 Residual ratio of DL-Tartaric acid after the reaction of ozone and hydroxyl radical with DL-Tartaric acid

Tartaric acid is a white crystalline diprotic aldaric acid. It occurs naturally in many plants, particularly grapes, bananas, and tamarinds, is commonly combined with baking soda to function as a leavening agent in recipes, and is one of the main acids found in wine. It is added to other foods to give a sour taste, and is used as an antioxidant. Salts of tartaric acid are known as tartrates. It is a dihydroxyl derivative of succinic acid. For the low molecular weight organic contaminants such as DL-Tartaric acid, we researched its decomposition behaviours, the results are shown as figure 7-5. Hydroxyl radical has high oxidation decomposition ability, so it can decompose DL-Tartaric acid more than 50%. But DL-Tartaric acid is difficult to be decomposed by ozone.

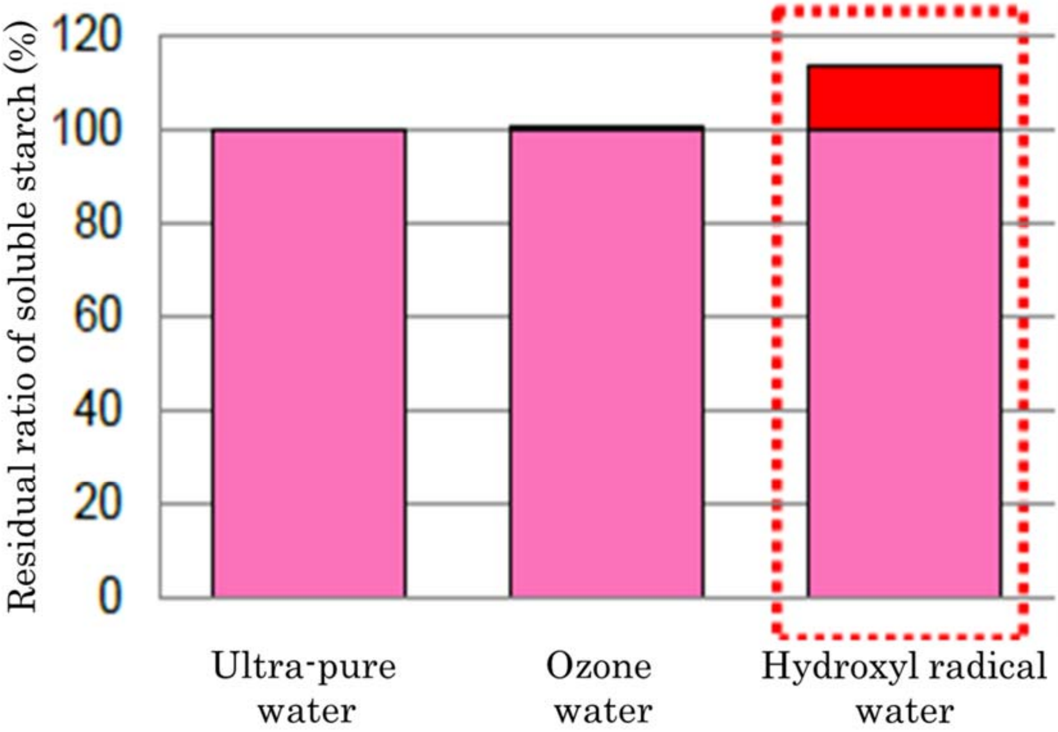


Figure 7-6 Residual ratio of soluble starch after the reaction of ozone and hydroxyl radical with soluble starch

Starch or amylum is a carbohydrate consisting of a large number of glucose units joined by glycosidic bonds. This polysaccharide is produced by most green plants as an energy store. It is the most common carbohydrate in human diets and is contained in large amounts in such staple foods as potatoes, wheat, maize, rice, and cassava. In this part, we can find that ozone can not react with soluble starch. Although it is possible that hydroxyl radical can reacts with soluble starch, it is difficulty. And Residual ratio of organic matter rises. It is shown as figure 7-6.

Like figure figure 7-7. Dioctyl phthalate and dibutyl phthalate belong to the class of phthalate esters and is used as an additive in many products including plastics, paints and inks or as a solvent in industrial formulations. The degradation of them in aqueous solution using ozone and hydroxyl radical was carried out in this study. Hydroxyl radical has a good removal effect, although it is almost the same to ozone removal effect.

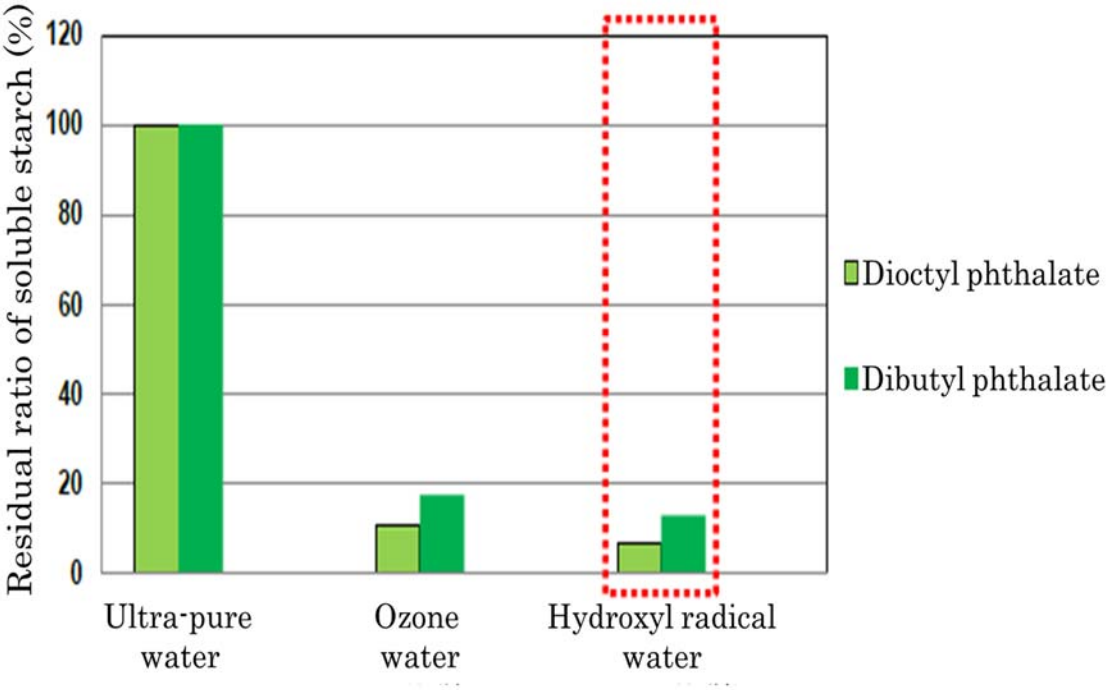


Figure 7-7 Residual ratio of phthalate after the reaction of ozone and hydroxyl radical with phthalate

7.3.3 Verify the oil contaminants decomposition effect

The precise instruments such as IC (integrated circuit) and semiconductor are easily contaminated by oil. But sometimes oil contamination is difficult to be treated by traditional treatment techniques using chlorine or ozone in the short time. Now we used hydroxyl radical water rinsing the oil, then observed the reaction interface, measured the solution turbidity after reaction between rinse water and oil to verify that hydroxyl radical water could achieve better effect than ozone-water for the mobile rinse in the short time. When we put the household lubricants into rinse water, the state is shown such as figure 7-8. The state of reaction for 20 min is shown such as figure 7-10 after reaction. Ultra-pure water still stayed transparent, and oil kept original state on reaction interface. Ozone water turned into milkiness, and generated white foam. hydroxyl radical water turned into milkiness, and generated white foam.

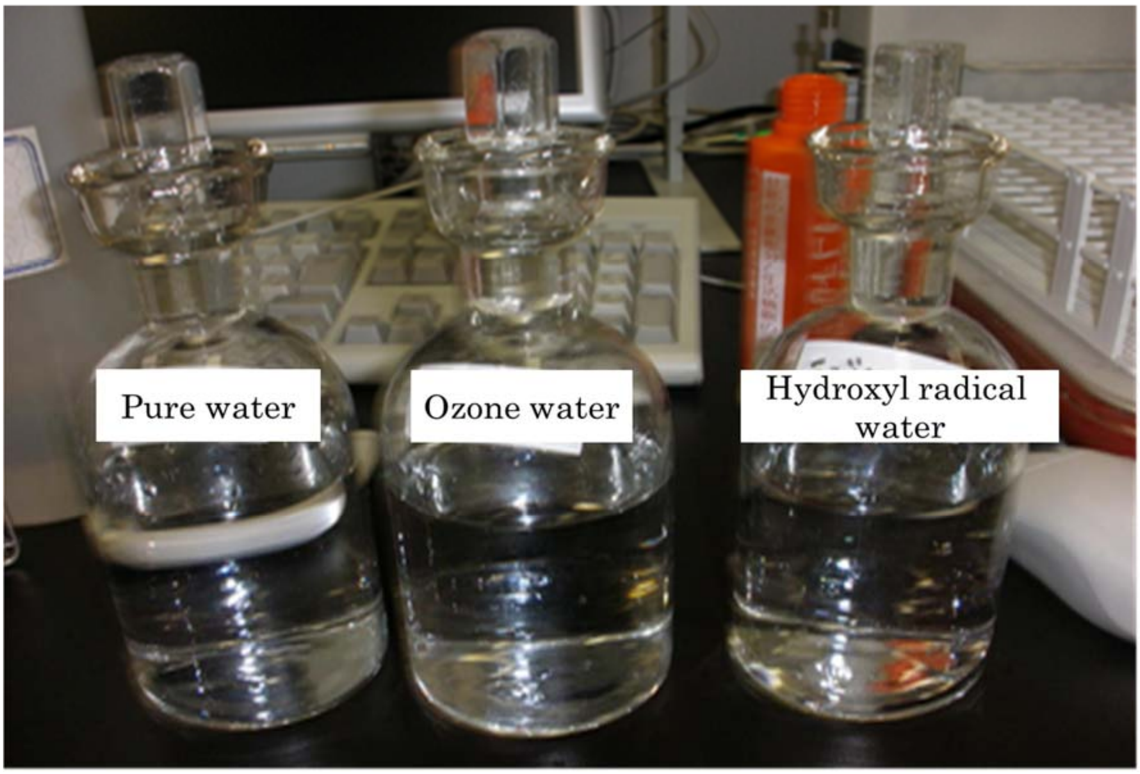


Figure 7-8 State of reaction, when we put the household lubricant into rinse water

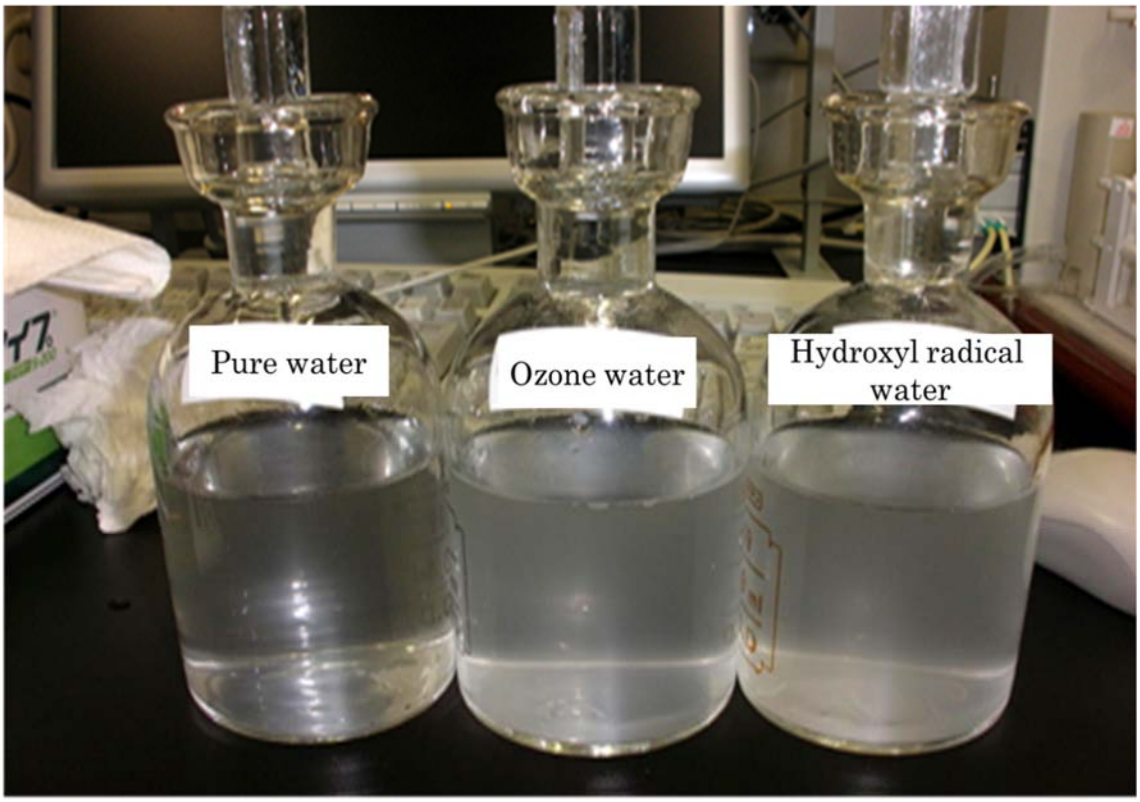


Figure 7-9 State of reaction between household lubricant and rinse water

The change of turbidity with time is shown such as figure 7-10 after reaction. The turbidity of ultra-pure water gradually decreased with time. The turbidity of ozone water kept no change with time. The turbidity of hydroxyl radical water had a little decrease with time. Generally, hydroxyl radical had a better effect than ozone water for oil rinse, and for hydroxyl radical water, the decrease speed of turbidity was more slowly than ozone. But in our experiment, ozone concentration is about 3~4 times more than hydroxyl radical concentration that was generated by the mobile hydroxyl radical rinse water equipment, so ozone water is better. In next step, we will do this experiment, under the same concentration of hydroxyl radical and ozone.

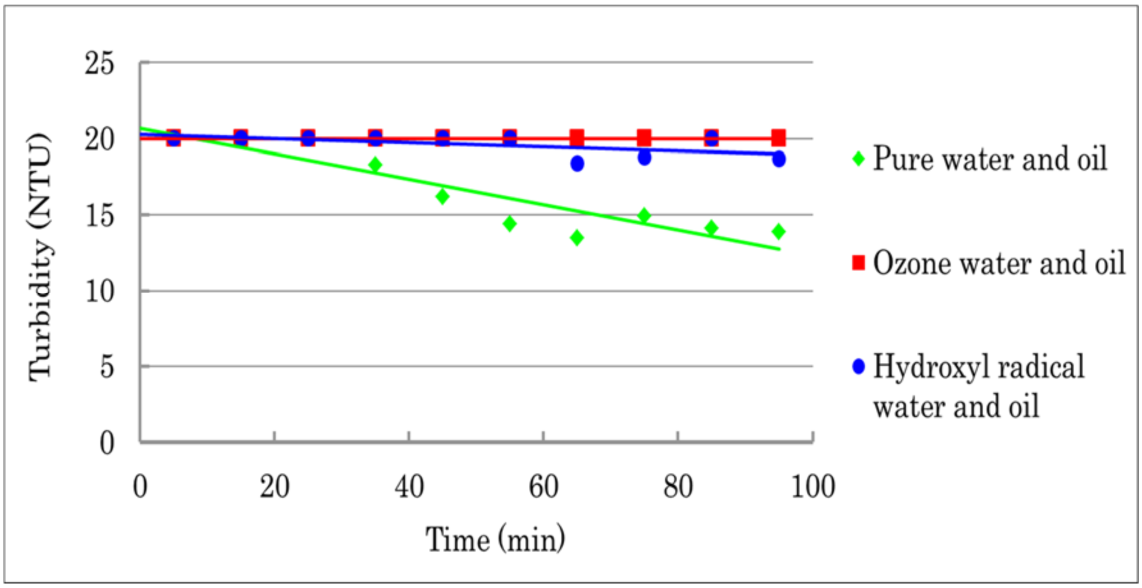


Figure 7-10 Change of household lubricant-rinse water reaction solution turbidity with time

7.4 Conclusions

In this study, the ionization effect of the metal impurities which is commonly found on the semiconductor surface in wafer and IC manufacturing processes, were investigated by using ozone, ultraviolet illuminating, low-megahertz ultrasonic and titania nanotube photocatalyst technique. Our results show that metal impurities, like Fe, Cu, Zn, Ag and so on, can be effectively and simultaneously reacted to form cation status by this new technique, if it is performed under optimal process conditions. Because these metal cations are easy to dissolve into water, we think this new technique can effectively achieve metal impurities removal's aim. And hydroxyl radical can deal with the metal impurities at the same time. The result of the paper has provided an important basis for the next stage of experiment research about metal impurities removal on the wafer surface using hydroxyl radical. In addition, the detection of hydroxyl radicals is not a trivial process. For this study, luminescence measurement was chosen, and luminescencer octa AB-2270 and UV absorption ozone monitor were combined together as a semi-quantitative and qualitative tool for the determination of hydroxyl radical from different systems. Here, it has been proven to be the most useful method about detecting hydroxyl radicals, due to its high sensitivity and high selectivity.

For the organic contaminants, the changes of CODMn of DL-tartaric acid (molecular weight: 150) and soluble starch after 2 days reaction with the reacted water sample were investigated. In case of DL-tartaric acid which is a relatively low molecular weight of organic compound, 10 and 18% of CODMn decreased for the primary O_3 water and the oxidizing substances except for O_3, respectively. In case of soluble starch which is a high molecular weight of organic compound, CODMn did not change for the primary O_3 water and 17% of CODMn increased for the oxidizing substances except for O_3. This shows that a part of soluble starch was converted to the oxidisable compound and the high molecular weight of organic compounds as carbohydrate, protein and lipid are not decomposed largely by the oxidizing substances except for O_3.

Although we have made great breakthrough in terms of hydroxyl radical generating technologies, some problems still remain unprocessed, such as the residual time of hydroxyl radical, application technology of hydroxyl radical and so on. We expect that hydroxyl radical will be better applied in the fields of environment, food safety and medicine.

Chapter Eight - Summary

Hydroxyl radical reaction is defined as the oxidation processes which generate very powerful, non-selective radical that are utilized in environmental treatment. Hydroxyl radical is comparatively new and intensively developing technique. Ozone-base hydroxyl radical is the process where ozonation is applied simultaneously with UV radiation, catalysts and ultrasound, which rely primarily on oxidation with hydroxyl radical. Such approach aims to improve and enhance the oxidation of contaminants such as metal, oil and organic matters. For environment and human, to lower the ozone consumption and energy cost; to improve the degradability of intractable organic matters, etc. Hydroxyl radical has high potential to degrade organic contaminants that are not attacked by ozone and chlorine. Ozone-based hydroxyl radical has developed from the laboratory to full-scale applications and is successfully used for environmental treatment like wastewater (has been applied successfully for the removal or degradation of toxic pollutants or used as pretreatment to convert recalcitrant pollutants into biodegradable compounds.) and wafer-cleaning techniques (it can provide practical benefits in the removal of photoresist, organics, metals, and particles on the wafer surface.). We generated high-density Hydroxyl Radical by the technology comprehensively using ozone, ultraviolet, ultrasonic and high light sensitive titania nanotube photocatalyst.

In order to better to apply hydroxyl radical, the formation of active intermediates from hydroxyl radical reaction with organic matter in aqueous solution has been investigated. We can treat environmental issues well after understanding these mechanisms.

In this study, the ionization effect of the metal impurities which is commonly found on the semiconductor surface in wafer and IC manufacturing processes, were investigated by using ozone, ultraviolet illuminating, low-megahertz ultrasonic and titania nanotube photocatalyst technique. Our results show that metal impurities, like Fe, Cu, Zn, Ag and so on, can be effectively and simultaneously reacted to form cation status by this new technique, if it is performed under optimal process conditions. Because these metal cations are easy to dissolve into water, we think this new technique can effectively achieve metal impurities removal's aim. In my paper, for organic matters, hydroxyl radical is also an ultimate oxidation tool — able to attack any molecule in their vicinity in order to balance their unpaired electron configuration. It can cut the organic C-C bond, and break double bonds (such as C=C, C=O, N=N and so on), degrade hydrocarbons, cause epoxidation and aromatic ring opening, radical polymerization, formation of secondary radicals and many other types of reactions. So, utilizing the strong oxidizing strength of hydroxyl radical, oxidation reaction is the most effective way of degrading and eliminating all kinds of pollutants and waste chemicals both in air and water. These have been proved by our experiments. In study, the most important point is that we can increase the life of hydroxyl radical. It took ~5 min for hydroxyl radical to return to its original state of water. This point will better help us to apply it for environmental treatment.

Hydroxyl radical plays a crucial role in different chemical and biochemical reactions. Hydroxyl radical causes several human diseases as it is having high reactivity with second order rate constants of $10^7 – 10^{10}$ L mol^{-1} s^{-1}. Hence, the detection of hydroxyl radical is essential. There are various methods reported for the detection of hydroxyl radicals. HPLC or GC is also used as a tool to quantify the products generated by hydroxyl radical targeting organic reagents. However, most of them involve highly technical analytical procedure using expensive solvents or chemicals. One of the most commonly used methods is ESR. However, the ESR measurement is having certain difficulties including tediousness, cost and stability. Firstly, the hydroxyl radical spin adduct formed is unstable, and may react with other species present in the system. Consequently the detection of Hydroxyl radical will be difficult. Secondly, ESR technique involves high cost instrumentation, which makes it unsuitable for routine analysis. Besides ESR measurement, other methods involve the use of different chemical probes like dimethyl methylphosphonate, 4-hydroxy benzoate, dimethyl sulfoxide, salicylate using HPLC analysis. These methods are also having disadvantages and diffuculties due to the formation of multiple hydroxylated products. The use of benzoic acid as a chemical probe for the detection of hydroxyl radical also has some difficulties, which include the formation of many hydroxylated products such as o-hydroxy, m-hydroxy, p-hydroxy benzoic acid, etc. such as o-hydroxy, m-hydroxy, p-hydroxy benzoic acid, etc. However, the formation of salicylic acid can be determined quantitatively by a simple colorimetric method. Salicylic acid forms a purple colored complex in the aqueous medium in the presence of Fe^{3+} ions. In the present study, the semi-quantitative determination of hydroxyl radical is responsible for the formation of chemiluminescence which is the generation of electromagnetic radiation as light by the release of energy from a chemical reaction. And chemiluminescent measurement has several advantages over other analytical techniques for hydroxyl radical detection. For example, extraordinary high-sensitivity, inexpensive instrumentation, cost-effective, easy operation with user-friendly menu driven software, speedy and stability. The developed method was not only useful for the detection of hydroxyl radicals in low level concentration, but also helpful to identify the optimal conditions for producing hydroxyl radicals and determination of generated hydroxyl radical count. Overall, the developed method could be used for the detection of hydroxyl radical produced by any system in general and this method had advantages due to its simplicity in instrumentation using less reagents/solvents, and it is cost-effective. Meanwhile accuracy had been proved by other methods.

So hydroxyl radical is very powerful oxidizing agent. They are involved in hydroxylation reactions, in biological and atmospheric phenomena. A recent application of these radicals is their use in chemicals removal that come from dioxins and dioxin-like compounds, PCB, pesticides, polymer additives and organohalogen compounds following chlorine element processing are causing serious environmental pollution, affects human health. We fully had discussed the feasibility of effect from hydroxyl radicals in water purification treatment and semiconductor wafer rinse. Furthermore, we are trying to use hydroxyl radicals in food sterilization and food safe handling in China, because it has very strong sterilization ability. In the field of process of water purification and food safety, we will try to explore the decomposition behavior of pesticide through using hydroxyl radical water to dispose the 20 compositions of pesticides. In addition, the hydroxyl radicals can be expected to handle these compositions of pesticides decomposition that is hardly to remove by ozone or chlorine element and the decomposition product will not cause secondary pollution in the process of water purification. In the field of food safety, hydroxyl radicals not only have the effect of decomposition to remove residues of pesticides, but also can achieve the purpose of sterilization. The hydroxyl radicals have damaging effects on bacteria, and it has small molecular weight, so it is without any damage to the food itself. So the hydroxyl radicals can also be looking forward to use in food safety field. In Japan, the safety of crops including contamination with agricultural pesticides is a major concern to both the producer and consumer, and the development of a method to remove the pesticides before marketing has been eagerly awaited. In Japan, about 600 agricultural pesticides are included in the Positive List established in 2010. Since agricultural crops cannot be marketed when they contain pesticides exceeding the residual limit, the development of a measure for eliminating residual pesticides in crops is now an important issue. Other applications include preventing electrostatic by hydroxyl radical; hydroxyl radical has a positive influence on plant growth and survival. Not only regulate plant growth and development but also increase plant resistance to various virus; in-situ soil and groundwater treatment technologies using hydroxyl radical. About hydroxyl radical, although we have a lot of research date, it is not enough. So, there are many deficiencies still need us to improve.

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Publications and Presentations

Publications:

1. HYDROXYL RADICAL RINSE WATER TECHNOLOGY USING OZONE ULTRASONIC ULTRAVIOLET AND TiO_2. Proceeding of 2011 International Symposium on Water Resource and Environmental Protection, IEEE PRESS Vol. 02.
2. Photodecomposition Behaviors of Pesticides in the Source for Water Supply Using an Alumina Carrier-Titanium Dioxide Photo-catalyst. FOOD INDUSTRIAL PROCESSES.
3. Characteristics and antibacterial activity of Ag-embedded Fe_3O_4@SiO_2 magnetic composite as a reusable water disinfectant. This journal is © The Royal Society of Chemistry 2013 RSC Adv., 2013, 3, 11751–11758.
4. Photo-decomposition of volatile organic compound using nano-reaction field separation TiO_2 photo-catalyst. Sustainable Environment Research, Vol.24, No.4,July 2014.

Presentations:

1. 2011 International Symposium on Water Resource and Environmental Protection, HYDROXYL RADICAL RINSE WATER TECHNOLOGY USING OZONE ULTRASONIC ULTRAVIOLET AND TiO_2.
2. Annual conference on ozone science and technology in Japan 2011
Development of Hydroxyl Radical Rinse Water Device and Evaluation of Rinse Effect.
3. Association of American Geographers' Annual Meeting, Los Angeles, California, 2013.
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