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**Studies of synthesis and photocatalytic properties of
TiO₂ films with various morphologies**

Duck-Hyun Song

In recent years, environmental concerns have grown globally. One of the most urgent environmental issues is the effective protection and utilization of the clean water resources of the world. Recently, a combination of population growth and the rapid development of industrialization has resulted in a steady rise in water pollution in many parts of the world due to the accelerated release of harmful agents. According to the World Health Organization, 768 million people lack access to safe drinking water, and 3.4 million people die annually from diseases transmitted through unsafe water.^{1,2} Furthermore, the number of persons with access to only unclean water resources could increase markedly in the short-term future, because of increasing water contamination due to large discharges of pollutants and contaminants into the natural water cycle.³⁻⁵

One of the major threats to human health is chemical pollution of water, such as by solvents, dyes, and pesticides.⁶ These chemicals in drinking-water have been shown to cause serious acute health problems in the short/long-term. To protect human health, and environment from water pollution, the development of advanced, low-cost, and high-efficiency purification processes to treat waste-water is desirable.

Conventional purification processes consist of a combination of physical, chemical, and biological methods. Generally waste-water treatment can be separated into four major treatment processes: preliminary, primary, secondary, and advanced.⁷ These conventional purification processes remove coarse solids and other large materials on preliminary treatment, settleable organic/inorganic solids and floating materials on primary treatment, residual organics and suspended solids on secondary treatment, and nitrogen, phosphorus, additional suspended solids, refractory organics, heavy metals, and dissolved solids on advanced treatment.

Unfortunately conventional waste-water treatment technologies cannot remove all

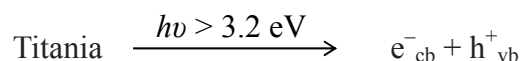
contaminants. The advanced oxidation processes have shown marked potential for the treatment of waste-water. This process can overcome the limitations of conventional technologies by the mineralization of toxic organic compounds. The rationales for these advanced oxidation processes are based on the *in situ* generation of highly reactive transitory species, such as hydrogen peroxide, hydroxyl radicals, superoxide radicals, and ozone, for the mineralization of refractory organic compounds, water pathogens, and disinfection by-products.⁸⁻⁹ Advanced oxidation comprises five kinds of process: ozonation, ultraviolet photolysis, fenton processes, electrochemical oxidation processes, and photocatalytic processes.

The photocatalytic process is emerging as a promising technology for the treatment of organic contaminants in environmental control. It has been widely established as an alternative physicochemical process for the elimination of toxic and refractory organic substances and metals in waste-water, drinking water, and air.¹⁰⁻¹² This attractive process has several advantages, including: (1) complete mineralization, (2) no waste disposal problem, (3) low cost, and (4) only mild temperature and pressure conditions are required.

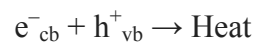
Among the many kinds of semiconductor for photocatalysts, titania is the most reliable material due to its marked photo-oxidizing potential, high chemical and thermal stability, nontoxicity, low cost, and strong mechanical properties.¹³ The principle of heterogeneous titania photocatalysis is as follows. Titania photocatalysis generates strong oxidizing power on illumination with UV light at wavelengths of less than 385 nm; a semiconductor is characterized by an electronic band structure in which the highest occupied energy band, called the valence band, and the lowest empty band, called the conduction band, are separated by a band-gap.¹⁴ The band-gap energy for a

semiconductor indicates the minimum light energy necessary to produce conduction band “electrons”, which, for example, can give rise to electrical conductivity and valence band “holes”, which are actually the absence of electrons. These holes can react with water to produce highly reactive radicals ($\bullet\text{OH}$). Both the holes and hydroxyl radicals are very powerful oxidants, which can be used to oxidize most organic materials. Photoexcitation with light of an energy greater than the band gap promotes electrical transfer from the valence band to conduction band, creating an electronic vacancy or “hole” at the valence band edge and forming an “electron” at the conduction band edge.¹⁵ The hole and electron can recombine on the surface or in the bulk of the particle in a few nanoseconds, or can be trapped in the surface states where they can react with a donor or acceptor.¹⁶ When the semiconductor is in contact with an electrolyte containing a redox couple, the Fermi level of the semiconductor moves to equilibrate with the potential of the redox couple.¹⁷ Charge carriers are driven to surface trapping sites either by diffusion or migration induced by the space-charge gradient. Thus, an adsorbed electron donor (OH , organic contaminants) can be oxidized by accepting a hole from the surface. In the conduction band, an adsorbed electron acceptor (O_2 , organic pollutants) can be reduced by the conduction band electron trap, suppressing electron-hole recombination. The superoxide radical (O^{2-}) thus formed is an effective oxygenation agent, attacking both neutral substrates and surface-adsorbed radicals and/or radical ions. The photodegradation scheme can be written as:¹⁸

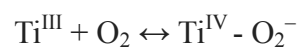
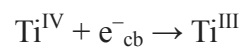
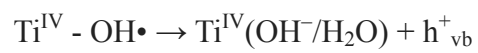
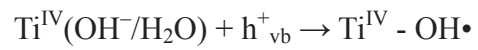
Excitation



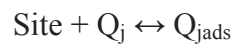
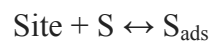
Back reaction



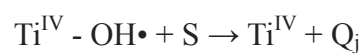
Trapping



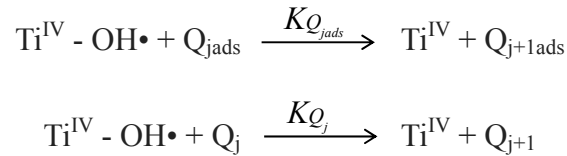
Adsorption of organic pollutant (S) and photogenerated intermediates (Q_j)



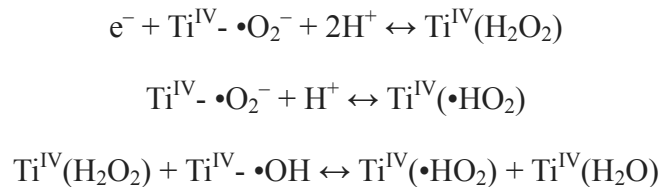
Hydroxy radical attack of the initial organic pollutant generating intermediates



Hydroxy radical attack of intermediates generating other intermediates



Other reactions



However, despite its many advantages and excellent photocatalytic properties, the traditional powdered titania still has limitations regarding its use in commercial photocatalytic processing. For example: (1) its photocatalytic efficiency easily decreases due to the aggregation of titania powders, especially when they are present at high concentrations; (2) separation of the titania powders from the suspension after the reaction is difficult; and (3) particulate suspensions are not easily applicable to continuous flow systems.¹⁹ In order to overcome these limitations, this research established an objective to decompose an organic compound, rhodamin B, using the titania films with various morphologies grown on a substrate.

First, single-crystalline anatase titania rods have been prepared on a glass substrate. The need for the growth of titanium dioxide rods on a substrate has directed attention to

the hydrothermal synthesis technique in wet chemical solution environments. Bin Liu²⁰ developed the hydrothermal method for the first time to grow oriented, single-crystalline rutile titania nanorod films on a fluorine-doped tin oxide (FTO) substrate for use in dye-sensitized solar cells. In a typical procedure, the same amounts of deionized water and hydrochloric acid are mixed in a Teflon-lined stainless autoclave. Then, the desired amount of titanium butoxide and a piece of FTO are placed in an autoclave. Hydrothermal synthesis was conducted at 220°C for 24 h in an electric oven. Bin and Eray were able to synthesize rutile titania nanorods with a fine diameter and uniform length on an FTO substrate. This method is very attractive for the growth of titania nanorod films. Subsequently, numerous researchers synthesized titania nanorod films on various substrates with the same hydrothermal method using dye-sensitized solar cells,^{21,22} self-cleaning antireflection,²³ and a UV sensor.²⁴ However, the success of hydrothermal synthesis depends on the selection of precursors that are both reactive and cost-effective, as well as appropriate process condition variables, which include the temperature, pH, and reagent concentrations. Especially, the growth of titania nanorods requires a large amount of a strong acid, hydrochloric acid, as a solvent. Therefore, it may cause environmental problems. Furthermore the hydrothermal process needs a special reactor, an auto-clave, due to the high pressure and high reaction temperature above the boiling point of the solution. In here, to vertically grow single-crystalline anatase titania rods on a glass substrate at mild, simple, and environmentally friendly experimental environment, a new glycolate process is proposed. This method, which is performed at an ambient pressure and with conventional glassware, could be adopted for a larger scale of production. Also, the glycolate complexes show good resistance to hydrolysis, and could be kept for several months without any precipitation in the

solution system. Nanostructures made of these glycolate precursors could not be dissolved using any known solvent. Furthermore, the developed glycolate process is considered to be a highly effective method for vertically growing metal glycolate rods, such as indium glycolate, zinc glycolate, and tin glycolate, with relatively mild experimental conditions and a simple process. By the new glycolate process, titanium glycolate rods have been successfully grown while vertically oriented on glass substrates. The obtained titanium glycolate rods have a uniform diameter and length. The diameter and length of titanium glycolate rods were controlled by changing the initial reactant concentration. On calcination, the titanium glycolate rods lost chemically bound organic compounds, and changed to anatase (500°C) and rutile (900°C) titania rods. The titanium glycolate rod has similar structure with anatase titania. Therefore, the titanium glycolate rods can be easily converted to anatase titania rods by calcination, while maintaining the rod morphology. The anatase titania rods exhibited marked photocatalytic activity, with photocatalytic degradation being 1.3 times higher than that with the commercial P-25 film.

Second, the silver core/titania shell nanowires have been prepared on a glass substrate via a glycothermal method. It is very important to prevent the recombination of photo-excited electrons and holes for enhancement of the photocatalytic properties of titania. Noble metals, including Pt, Au, Pd, Rh, Ni, Cu, and Ag, have been reported to be very effective to prevent recombination.²⁵⁻³¹ The Fermi levels of noble metals are lower than those of titania; therefore photo-excited electrons can be transferred from CB of titania to metal particles, which are deposited in the surface of titania, while photo-generated VB holes remain on the titania. These activities reduce the possibility of electron-hole recombination. Anpo and Takeuchi reported on electron spin resonance

signals when investigate electron transfer from titania to Pt particles.³² According to their article, the loading of Pt on titania reduced the Ti^{3+} signals. This observation indicates the occurrence of electron transfer from titania to Pt particles. As electrons accumulate on the noble metal particles, their Fermi levels shift closer to the conduction band of titania.³¹ Accumulated electrons on metal particles can be transferred to protons adsorbed on the surface and further reduce the protons to hydrogen molecules. Therefore, noble metals with suitable functions can help with electron transfer, leading to a higher photocatalytic activity. However, the continual use of a photocatalyst made up of noble metals to reduce the recombination of photo-excited electrons and holes soon leads to a decrease in photocatalytic properties as the noble metals are quickly dissolved in the medium used.³³ To overcome this problem, silver core/titania shell-structured nanowire is fabricated via a glycothermal method assisted by a photochemical reaction. By a photochemical reaction, silver ions form decahedral silver in a favorable geometry. At the glycothermal condition, titania coats the silver decahedron and act as a template, which results in anisotropic growth to form one dimensional silver core/titania shell nano wire. The morphology, diameter, length, and density of the core/shell nano-wires that were synthesized could be varied by changing the silver/titanium molar ratio of the starting materials. The silver core/titania shell nano-wires show superb photocatalytic properties, with photocatalytic degradation being 1.7 times higher than that with the commercial P-25 film.

Lastly, the three-dimensional titania building blocks have been prepared on a glass substrate. The three-dimensional titania building blocks have a large surface area and show sufficient space between the spherical titania powders. This large surface area increases opportunities to degrade waste-water, and the space between spherical

powders makes the chemical reaction proceed much easier because of reactant and product molecules moving in or out of the titania powders. Thereby, the three-dimensional titania building blocks are expected to exhibit marked photocatalytic properties. To fabricate the three-dimensional titania building blocks, the mono-dispersed titanium glycolate sphere powders were synthesized using titanium glycolate solution as a reactant and acetone as a solvent. Adding a surfactant, poly(oxyethylene) nonylphenyl ether, is highly effective at controlling the size distribution of titanium glycolate sphere powders. The three-dimensional titania building block films were fabricated by solvent evaporation method using synthesized titanium glycolate sphere powders and titania nano-powders. The titania films fabricated with various morphologies can be successfully converted to anatase phase titania by calcination at 500°C. The titania films showed excellent photocatalytic properties and stable durability for the decomposition of RhB under UV-light. The titania films are anticipated to be applicable for the continuous flow waste-water treatment system.

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