Utilization of new TiO_2 photocatalyst in purifier for removal of hazardous wastes

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Recently, various environmental problems are emerging due to the industrialization-oriented society and the reckless use of chemical fuels, and many eco-friendly studies are being conducted to solve them. The environmental problem have to be firstly solved is the air pollutants contained in industrial and car emission, which is a major cause of global warming. As representative air pollutants, volatile organic compounds (VOCs) are very harmful to human health and the environment. For example, benzene, formaldehyde and acetaldehyde (ACT) can cause headaches, vomiting and dizziness if they come in contact with the skin or enter the respiratory tract. In addition, these environmental problems should be urgently solved because they are harmful substances that can cause damage to the nervous system when exposed to high concentrations. In recent years, a lot of researches have been studied to effectively and rapidly remove the VOCs, such as adsorption, thermal oxidation, photocatalytic oxidation, and biofiltration. Among them, photocatalysts have been many studied because they show a very environmentally friendly aspect of producing water and carbon dioxide as a final by-product. In addition, photocatalyst materials have the advantage that they can be activated even with only solar energy. Resolving energy shortage and environmental pollutions problems has emerged as the most urgent challenge nowadays. As one of many solutions, using catalyst can lower activation energy of the reaction and produce more energy for us to use. Among the various catalysts, photocatalysts having the advantage of being more environment-friendly and utilizing light source have been studied. There are three main reasons why many studies of photocatalyst are conducted up to now. First, unlike other catalysts that react at high temperatures, they can have activity at room temperature. Second, the photocatalytic reaction can be induced through the utilization of light, which is an infinite resource. And finally, the photocatalytic reaction can be stopped by blocking the supply of light at a desired point in time. Given these points, photocatalysts seem to play an important role in solving future environmental issues such as global warming and energy saving.

Titanium dioxide (TiO_2), a well-known semiconductor, is the most widely used photocatalyst material due to its strong oxidizing power and excellent durability. Also, it is widely used for solar energy conversion applications such as solar cell by utilizing the inherent band gap of TiO_2. However, TiO_2 has a band gap of about 3.0 to 3.2 eV that can only absorb UV-light. Since most of the light energy is visible-light, in order to effectively utilize the light source, it is important to develop a photocatalyst having an activity in visible-light. Many studies have been performed to overcome this problem. A typical method of tuning a band gap is by doping a metal or non-metal to TiO_2 and coupling with semiconductor having a narrow band gap. Although such photocatalyst material with visible-light activity has increased wavelength range to be absorbed, it also has several disadvantages. For example, the experimental process is very complicated, requiring high temperature and high pressure. In addition, these materials have low photocatalytic efficiency in visible-light. In recent years, researches have been conducted to form peroxo groups (Ti-OOH, -Ti-O-O-Ti- and -O-Ti-O-) by oxidizing metal oxide surfaces through H_2O_2. Because peroxo complex has a visible-light activity, it can lead to transfer of electrons to conduction band of metal oxide, resulting in formation of superoxide anion. Generating metal oxide with a peroxo surface is a relatively simple process. In addition, such metal oxide with peroxo surface has excellent visible-light photocatalytic efficiency that can be applied to various fields. Another study has been made to synthesize photocatalysts with visible-light activity by intentionally making oxygen vacancies in the TiO_2 lattice. For example, hydrogenated TiO_2 with oxygen vacancy can be synthesized by adding a strong reducing agent such as $NaBH_4$ to TiO_2. And studies have been reported on the synthesis of Ti^{3+} self-doped TiO_2 through hydrothermal method using $TiCl_3$ and $(NH_4)_2TiF_6$ as the precursor of Ti^{3+} and Ti^{4+}, respectively. The reason why these photocatalysts have visible-light activity is that oxygen defects in the synthesized titania based photocatalysts form a new donor level in the band structure and ultimately allow absorption of visible-light wavelength range.

In this study, amorphous Ti-based hydroperoxo complex (THPC) was successfully synthesized by a facile method only using titanium hydride (metallic Ti) and H_2O_2 under mild conditions. TiH_2 is known to have many more reactive sites than metal oxides such as TiO_2. Therefore, TiH_2 was selected as a precursor and Ti based peroxo complexes were successfully synthesized for the first time. During the synthesis method, polymerization was induced through exothermic reaction without any annealing process, resulting in formation of THPC with various colors such as green and yellow. Qualitative and quantitative analyses through various optical measurements revealed that the synthesized THPC had many peroxo groups and various oxidation states of Ti (Ti^{2+}, Ti^{3+} and Ti^{4+}).

Figure 1. Scheme illustration of the formation mechanisms of THPC photocatalysts.

Under visible-light irradiation, decolorization of Rhodamine B (RhB) as an organic dye and VOCs was performed to confirm how the hydroperoxo group and oxygen vacancy of THPC affect visible-light catalyst. The photocatalytic properties of successfully synthesized THPC show very fast organic decolorization rates, unlike other conventional visible-light catalysts. This is possible because many peroxo complexes can form more active radicals. Therefore, degradation experiments of VOCs such as formaldehyde and acetaldehyde (ACT) in a gas phase as well as phenol in liquid (water) phase were also carried out. Finally, a recycle test was conducted, one of the important items in the photocatalytic experiment as well as commercialization. That's why we did fabricate a filter system in a purifier by adapting synthesized THPC, and then successfully removed the VOCs. Based on this study, we suggested a possible photocatalytic oxidation mechanism of THPC as followings.

As we can see in the figure 2, when the hydroperoxo group absorbs visible-light, radicals are formed and e^- is formed by combining with an unshared electron pair of oxygen. The formed e^- reacts with oxygen in the air to form superoxide anions and provide strong oxidation. The remaining plus-charged hydroperoxo groups react with the water molecules on the surface to form OH radicals, which degrade the contaminants through reduction. For these reasons it can be demonstrated that the adsorption and degradation of ACT proceeds rapidly on the surface of THPC particles. And based on these characteristics, THPC samples are likely to be applied to future environmentally friendly applications that emphasize both efficiency and durability.

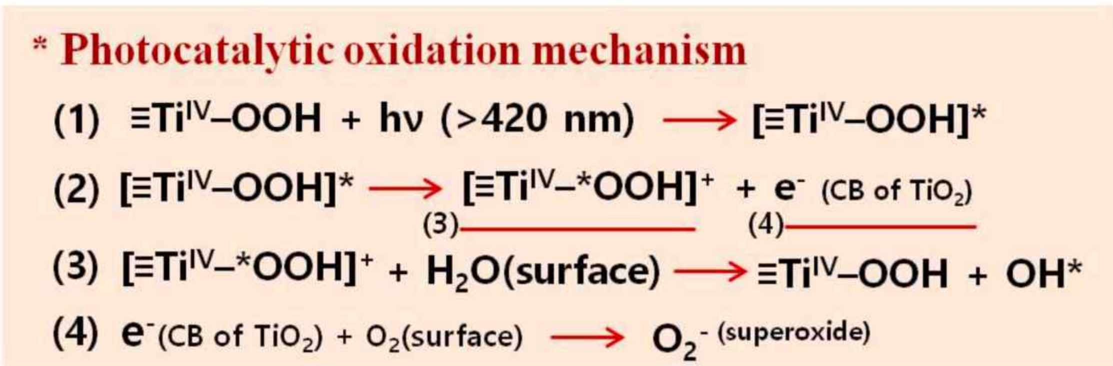

Figure 2. Photocatalytic oxidation mechanism of THPC.

From above results, we made a conclusion that all synthesized samples have been found to have good degradation efficiency because of many active carriers formed from the hydroperoxo group and oxygen vacancy of THPC. Overall data suggest that this study is a very good approach to solving the air pollution problem such as VOCs. The reason is that in the process of synthesizing THPC, not only low-cost precursors were used but also a facile synthesis method at room temperature was proposed. And the synthesis method is expected to be applicable to various fields as a scale-up synthesis method. In addition, it has the advantage that additional heat and pressure are not required during the synthesis process. This mild synthesis method will be a very valuable research if applied to other metallic materials besides TiH_2, and it will be easy to build a mass synthesis system in industrial aspect later.