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Article / Book Information

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著者(和文)	CABRAL Kerry Pan
Author(English)	Kerry Pan Cabral
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論 文 要 旨

THESIS SUMMARY

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学生氏名： Student's Name	CABRAL, Kerry Pan	指導教員（主）： Academic Advisor(main)		日野出洋文
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要旨（英文800語程度）
Thesis Summary（approx.800 English Words ）

One of the serious causes of water pollution comes from dye manufacturing and dye-consuming industries such as cosmetics, food, paper, plastics, and textile among many others. It has been estimated that 15% of produced dyes worldwide is lost in wastewater during the synthesis and processing. Even in small amounts (< 1 mg L^{-1}), dyes are clearly visible and can affect the water environment. Moreover, majority of the dyes produced nowadays are synthetic. Synthetic dyes, composed of complex aromatic molecular structures, are chemically stable and recalcitrant in nature. When present in surface waters, dyes could prevent sunlight penetration and aeration of the water body, which in turn inhibits the aquatic plants to photosynthesize. This could directly affect marine life, and eventually humans. When dye effluents are used for irrigation purposes, it causes death of soil microorganisms that could have an influence on agricultural productivity. Hence, it is necessary to treat water contaminated with dyes.

Titanium dioxide, TiO_2, is considered as the most promising photocatalyst due to its excellent features such as high photocatalytic activity, chemical stability, low toxicity, and low cost. However, its practical application is still hindered due to its wide band gap (~3.0-3.2 eV) and difficulty of separation in the liquid phase when used in fine powder form. In this research, three-dimensional (3D) sea urchin-like anatase TiO_2 (SUT) was synthesized using hydrothermal technique at 180 ℃ for 12 h, in the presence of a relatively green solvent such as ethylene glycol (EG) that acts as morphology directing agent in basic medium (1 M NaOH). The growth and formation mechanism for the as-synthesized SUT was systematically investigated by varying the hydrothermal reaction time. It was found that the primary particles of TiO_2 agglomerate to form larger structures with rough surface and then proceed with the development of spindle-like structures that surrounds a core. Moreover, it was revealed that it is only with the combination of NaOH and EG with hydrothermal treatment that the 3D TiO_2 structures could be formed. Without hydrothermal treatment, agglomerated TiO_2 particles formed. Calcining the SUT is necessary since the crystallite phase formed for the dried samples after the hydrothermal treatment is hydrogen titanate, which is often considered amorphous. In addition, calcination has an effect on the morphology of the samples that is why exploration of its influence on the SUT is necessary.

The calcination temperature was varied from 350, 550, 750, and 950 ℃. It was found that the crystallite phase changed from hydrogen titanate (no calcination) to anatase (350 and 550 ℃), then to mixed phase of anatase and rutile (750 ℃) until pure rutile phase was formed (950 ℃). Among the crystallite phases of TiO_2, it is well established that the anatase is the most photocatalytically active. There was no significant change in the morphology observed except for the sample calcined at 950 ℃. Meanwhile, the specific surface area of the samples decreased as the calcination temperature was increased due to sintering. The photocatalytic activity of the fabricated samples was tested towards the degradation of 20 mg L^{-1} methylene blue (MB) aqueous solution under natural sunlight irradiation. Results revealed that the sample calcined at 350 ℃ has the highest % MB degradation and is comparable with the performance of commercially available TiO_2 products such as Degussa (Evonik) P25 and Wako anatase TiO_2. The performance of the sample calcined at 350 ℃ was attributed to the synergistic effects of its unique sea urchin-like morphology, anatase crystallite phase, large specific surface area, and pore volume. Mineralization of MB was verified by performing chemical oxygen demand (COD) test. Moreover, it was found that the micrometer-sized superstructure of the as-synthesized SUT is easier to

separate by sedimentation as compared with the nanometer-sized particles of Degussa (Evonik) P25 and Wako anatase TiO_2.

Doping TiO_2 with either metal or non-metal ions has been done in order to reduce the recombination of photogenerated e^- and h^+, and to broaden its light absorption towards the visible light region. The impurities added to TiO_2 exhibit different effects since their interaction with the charge carriers vary depending on their position in the host lattice, ionic radii, concentration, and the synthesis method. In this study, a rare-earth metal was used as dopant to the as-synthesized TiO_2 sample. Only very few studies investigate holmium (Ho) as dopant to TiO_2. Ho-doped TiO_2 samples were previously reported to have smaller crystallite size, larger specific surface area, and extended light absorption. The Ho impurity could act as electron scavenger and can also concentrate contaminants on the surface of TiO_2. All these factors could contribute to the enhancement of photocatalytic activity of Ho-doped TiO_2. The effects of both dopant amount and calcination temperature on Ho-doped TiO_2 are essential in this study. It was found that the addition of Ho did not affect the morphology but decreased the crystallite size leading to a significant increase in the specific surface area. Compared with the undoped sample, Ho-doped TiO_2 has higher photocatalytic activity as it has larger specific surface area to concentrate MB molecules on the surface of TiO_2 prior to degradation. Furthermore, the Ho impurity could serve as an electron trap that prevented the recombination of photogenerated e^- and h^+ species resulting to higher photocatalytic activity. It has comparable performance with commercially available TiO_2 products such as Degussa (Evonik) P25 and Wako anatase TiO_2. Due to its 3D micrometer-sized superstructure, it is also easier to separate from the liquid phase after the treatment as revealed by the sedimentation test results.

The findings of this research could be used as future reference for the design of an efficient and eco-friendly photocatalyst for water treatment.