Thesis Summary

Mechanochemical synthesis of visible-light-active TiO_2 photocatalysts: relation between photocatalytic activities and disorder structures
（可視光応答型酸化チタン光触媒のメカノケミカル合成：触媒活性と乱れた構造の相関）

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General introduction

Titanium dioxide (TiO_2) is the most popular photocatalyst and is used for self-cleaning and self-sterilization applications, water and air purification, and as a water-splitting catalyst. TiO_2 photocatalyst is activated by UV light due to its wide band gap (3.0~3.2 eV, $\lambda \leq 387.5$ nm). Visible-light activated TiO_2 has attracted much attention using metal-ion or non-metal doping. However, almost all synthesis methods have required specific experimental conditions, such as ion-implantation facilities, vacuum, and high temperatures up to 400-800 °C for several hours.

A mechanochemical synthesis method has emerged as alternatives to modify TiO_2, because large amount of particles can be easily obtained by simply grinding solid materials in a milling vessel with milling balls. High-energy ball milling method is a useful approach to prepare TiO_2 particles, because large amount of particles can be easily obtained by simply grinding solid materials in a milling vessel with milling balls at room temperature. In fact, mechanochemistry was identified by IUPAC as one of ten world-changing technologies in 2019. In this study, we clarified the crucial factors governing the properties of photocatalysts and successfully designed high efficient TiO_2 photocatalysts via mechanochemical synthesis.

Chapter 1. Mechano-synthesized orange TiO_2 shows significant photocatalysis under visible light

Nitrogen and carbon co-doped TiO_2 particles with a brilliant yellow-orange color were produced mechanochemically by high-energy ball milling as one-pot synthesis. This facile synthesis required only grinding TiO_2 with melamine at room temperature. Using monochoromatic lights with the same intensity, the photocatalytic activity of the TiO_2 samples was evaluated with respect to the degradation of methylene blue (MB) solution. The activities under visible light (450 and 500 nm) were, respectively, 4 and 2 times higher than that of the pristine TiO_2 under UV light (377 nm). The properties and structure of the co-doped TiO_2 particles before and after milling were analyzed using eight experimental methods. As a result, it was found that the nitrogen replaced as an oxygen site in milled TiO_2 has the highest concertation (2.3%) in the past studies and the structure of milled TiO_2 is composed of a polymorphism of four different solid phases of TiO_2. A good repeatability of the photocatalyst was investigated by the number of cycles for the decomposition reaction of the aqueous dye solution.

Chapter 2. Mechanochemical Synthesis of Red-Light-Active TiO_2 Photocatalysts: Four Colors, Defect-Rich, Polymorphism, and No Metal Loading

Herein we report the syntheses of four colored TiO_2 photocatalysts, green, gray, orange, and yellow, via a mechanochemical method (Table). All four colored TiO_2 samples, which had absorptions in the UV-vis-NIR regions. The densities of the defects, oxygen vacancies, and Ti^{3+} in TiO_2 were quantified and were used to evaluate the photocatalytic activity in conjunction with the contents of the four polymorphic phases, i.e. anatase, rutile, TiO_2 Ⅱ, and amorphous phases. Green and orange TiO_2, which contained all four phases and had high densities of dopants and oxygen vacancies, exhibited a 5-fold enhancement of the photocatalytic activity with respect to that of P25. According to the action spectrum of the reaction rate constant, red light from around the NIR region was vital in enhancing the photocatalytic reaction. Furthermore, all the prepared TiO_2 photocatalysts did not need promoters nor metal-loading in the reaction.

Chapter 3. Two-step mechanochemical synthesis of disordered green TiO_{2-x} photocatalyst

To produce TiO_2 photocatalyst with rich and stable oxygen vacancies and Ti^{3+}, it is better to separate one-pot milling to two steps milling. The first step is TiO_2 ball milling in inert ambient to produce the Vo and Ti^{3+} earlier. Then, the second step is mechanochemical doping N or C elements on the disordered surface of TiO_2, so that the doping level is deeper and more stable. The present study investigated the photocatalytic activity of the TiO_2 particles prepared by two steps milling. The size, morphology, crystal structure, electronic structure of bonding and spin density of TiO_2 particles as functions of milling time compared to one-pot milling were evaluated by five different measurements.

General conclusions

1) The significant enhancement of TiO_2 photocatalytic activity was observed by adjusting the amount of added melamine in ball-milling. The electronic structure, bandgap energy (Eg) and the wavelength of light absorption, polymorphism, and disorder of the TiO_2 particles could be controlled in specific milling condition, which are also the important factors of photocatalytic activity enhancement.

2) It is the first time to design and synthesize the full UV-vis region active TiO_2 photocatalyst without metal loading, by milling P25 with melamine in argon ambient, which shown significant enhancement of photoactivity than the pristine TiO_2. The photocatalyst with color of green is the most efficient sample. High photocatalytic activity is present in samples with a defect density > 4×10^{18} mol^{-1} and an absorption area > 300 (Art. unit).

3) Based on the one-pot ball-milling method, a two-step milling method was used for green TiO_2 synthesis. The synthesized disordered TiO_2 photocatalyst was more stable that keeping Vo and Ti^{3+} for over 2 years.