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Titanium dioxide modification with cobalt oxide nanoparticles for photocatalysis

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ABSTRACT

Liquid phase plasma (LPP) method was used to synthesize a photocatalyst that can respond to visible light by precipitating cobalt oxide nanoparticles on the surface of TiO_2 powders. Uniform precipitation of cobalt oxide nanoparticles on the surface of TiO_2 powders was observed, resulting in successful synthesis of Co oxide nanoparticles on TiO_2 photocatalysts (CTP). The CTP synthesized in this study showed a photocatalytic activity under visible blue light. However, its photocatalytic activity was lower than that of bare TiO_2 under UV light because the cobalt oxide precipitate acted as crystal defects deteriorating the catalytic activity.

Introduction

Titanium dioxide (TiO_2) is a cheap metal oxide with superior photocatalytic properties and chemical durability. Since its photocatalytic properties were discovered in 1972 by Fujishima-Honda research team, TiO_2, which had been used exclusively as white pigment before, has been widely used as basis materials for manufacturing sunscreen, photocatalyst, and solar cell [1]. Because of relatively large band gap of this compound (e.g. 3.2 eV for anatase), it has to absorb ultraviolet (UV) rays to exert photocatalytic activity or to act as solar cell. However, the solar energy that TiO_2 can utilize is very limited for two reasons. Firstly, the portion of UV energy in the total solar energy is less than 5%. Secondly, all the UV energy is not used because the quantum efficiency of TiO_2 is low. This hinders wider use of TiO_2 in solar energy applications. Efforts have been made to develop new photocatalysts that can use visible and near-infrared lights, which account for more than 60% of total solar energy, with high quantum efficiency. The simplest way to realize this is to alter TiO_2 so that it can utilize visible and near-infrared with high quantum efficiency [2–10].

A liquid-phase plasma (LPP) method using glow discharge in liquid was recently suggested as a promising method to synthesize metal nanoparticles [11,12]. The strength of the LPP method is very high reaction rate due to activated species and radicals produced under high pressure. Because of the reaction field with an excited energy state formed by LPP, the addition of reducing agents is not required in an LPP process.

In this study, we evaluated a new material, Co oxide nanoparticles on TiO_2 powder, to reduce the large band gap of pure TiO_2 powder (P25). To investigate the structural effect of the catalyst on photocatalysis, Co oxide nanoparticles on TiO_2 photocatalysts (hereafter CTP) with anatase and rutile structures were prepared using an LPP method. This method offers cobalt nanoparticles impregnation in a single-step process. The photocatalytic activity of CTP was investigated with decomposition of dye in its aqueous solution.

Experimental

Materials

The titanium dioxide used in this study was Degussa P25 (ca. 80% anatase, 20% rutile, with a BET surface area of 50 m^2/g and an average particle size of 25 nm). All the chemicals used in this work were of reagent grade and used without any further purification.

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Cobalt chloride hexahydrate ($CoCl_2{\cdot}6H_2O$, Daejung Chemicals & metals Co., Ltd) was used as the precursor to produce cobalt nanoparticle using the LPP method. Cetyltrimethylammonium bromide (CTAB, $CH_3(CH_2)_{15}N(CH_3)_3Br$, Daejung Chemicals & metals Co., Ltd) was used as the dispersant to enhance the dispersion of and to avoid the coagulation between cobalt particles produced in aqueous solution during the LPP reaction. Ultrapure water (Daejung Chemical & metals Co. Ltd.) was used as the solvent for the LPP reaction and the decomposition reaction. Acid orange 7 (AO7, $C_{16}H_{11}N_2NaO_4S$, Aldrich Co. Ltd.) was used as the model pollutant to decompose in the evaluation of photocatalytic activity of the synthesized CTP.

Apparatus

CTP was prepared using the LPP apparatus. Similar apparatus was used in our previous study to generate nanoparticles dispersed in an aqueous solution using the LPP process [13]. Detailed information of the experimental setup can be found in that paper [13]. Fig. 1 shows the schematic of the experimental apparatus used in this study to evaluate the photocatalytic activity of CTP. An LED light module was prepared by installing 100 UV-LEDs (Nichia corp., NSPU510CS) and 100 Blue-LEDs (Nichia corp., NSPB510BS) with regular intervals inside a cylindrical plastic pipe with an inner diameter of 45 mm and a height of 120 mm. A light control box was used to control the intensity of radiation supplied to the decomposition reactor by switching on–off the LED lamps of the LED light module. The decomposition reaction was carried out by circulating the AO7 solution with dispersed CTP between a reactant tank and a quartz reactor (Φ = 22 mm, height = 220 mm) with a constant flow rate using a metering pump.

Preparation of CTP

CTP was generated by the LPP process. The LPP is defined as a discharge in aqueous solution, stabilized by the exchange of electrons and ions between gas and liquid phases. This liquid plasma generates a number of highly active species in the aqueous solution. The reactants of the desired reaction are added into the solution and they react with the active species, e.g. hydrogen, oxygen, and hydroxyl radicals, at the interface of gas and liquid phases. The Co nanoparticle production using the LPP method via the reduction of metal ions and hydrogen radicals was found to be an effective process [14].

An LPP system with a high frequency bipolar pulse-type power supply (Nano technology lnc., NTI-1000 W) was used for the reduction of cobalt ions dissociated from cobalt chloride. The power supply was operated under a pressure of 250 V, a frequency of 30 kHz, and a pulse width of 5 μm. Electric power was supplied into the double tube type LPP reactor through tungsten electrodes installed in both sides of the reactor with a distance between them of 1.0 mm. In order to synthesize CTP using the LPP method, 5 mM of $CoCl_2{\cdot}6H_2O$ and 2.5 mM of CTAB were dissolved in 250 mL of ultrapure water and then 0.5 g of TiO_2 powders (P25) were added. The mixture was stirred for 10 min for uniform dispersion and introduced into the LPP reactor. CTP was produced by operating the LPP process for 90 min to precipitate cobalt nanoparticles on the surface of TiO_2 powders. After the completion of the LPP reaction, the reaction solution underwent centrifugation (4000 rpm) and washing repeated five times each to remove remaining chemicals and CTAB. The precipitate was dried for 48 h in a vaccum oven maintained at 353 K. The elemental composition of the synthesized CTP was analyzed using a Field Emission Scanning Electron Microscope (FESEM, JSM-7100F, and JEOL). A High Resolution Field Emission Transmission Electron Microscope (HR-FETEM, JEM-2100F, JEOL) was used to examine the elemental distribution of the particle surface. X-photoelectron spectroscopy (XPS, Multilab 2000 system, SSK) was used to analyze the chemical composition of CTP. UV–vis spectroscopy (Avantes AvaLight-DHS) was used to measure the band gap energy of CTP.

Evaluation of photocatalytic activity

Experiments were performed to evaluate the photocatalytic degradation of AO7 by using a re-circulation-type reaction system with UV or visible light LED lamps. CTP was mixed with 600 mL of AO7 solution with an AO7 concentration of 1.38×10^{-2} mg/L. This reactant solution was circulated between the reactant tank and the quartz reactor installed inside the LED light module using a metering pump to allow photocatalytic decomposition of AO7. Samples were collected from the reactant solution with a uniform time interval. After centrifugation, the samples were passed through a 0.2 μm syringe filter to remove CTP. The AO7 concentration of the samples was determined by measuring their absorptivity at λ max = 485 nm using a UV–vis spectrometer (UV-1601, Shimadzu). The experimental conditions are as follows: reaction temperature of 293 K, pH of 6.17, and reaction time of 350 min.

Results and discussion

Characteristics of the CTP

Fig. 2 shows the energy-dispersive X-ray spectroscopy (EDS) spectrum for the CTP synthesized using the LPP method. The two elements comprising TiO_2 powder (P25), titanium, and oxygen

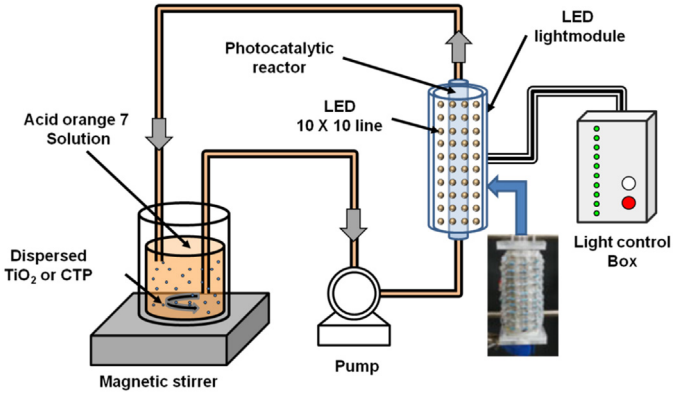

Fig. 1. Schematic diagram of photocatalytic degradation experimental apparatus with LED light.

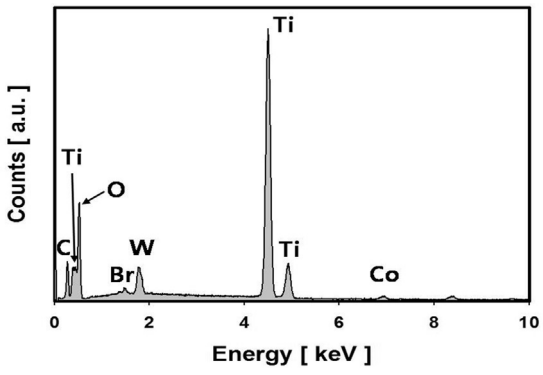

Fig. 2. EDS spectrum of CTP prepared by LPP method.