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Characterization and photocatalytic activity of K^+-doped TiO_2 photocatalysts

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Abstract

Titanium dioxide doped with K^+ up to 14.3 at.% was prepared by the sol–gel method and thermal treatment. The prepared samples were characterized and subjected to photodegradation of Everdirect Supra Blue BRL dyes (BRL). A mixture of various titanates, $K_{4-4x}Ti_xO_2$, was recognized for the increase in photocatalytic activity. Doping K^+ decreases the crystal size of titanium dioxide, decreases the diminishing rate of surface area with calcination temperature, and increases the calcination temperature required to attain the optimum photocatalytic activity of the sample. TiO_2 doped with 4.6% K^+ and calcined at 973 K shows much higher photoactivity than the other samples when the doping level of K^+ and calcination temperature are 0–14.3% and 673–1273 K, respectively. Photocatalytic degradation of BRL follows the Langmuir–Hinshelwood adsorption model, and the adsorption equilibrium constant and rate constant are 0.0072 min^{-1} and 3.01 ppm/min, respectively. The reaction takes place much effectively at pH 7.2.

Keywords: Titanium dioxide; Potassium ion; Doping; Photocatalytic; Dye

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1. Introduction

Semiconductor photocatalysis has been investigated extensively for light-stimulated degradation of pollutants, particularly for complete destruction of toxic and non-biodegradable compounds to carbon dioxide and inorganic constituents [1–4]. Several semiconductors exhibit band-gap energies suitable for photocatalytic degradation of contaminants. Among the photocatalysts applied, titanium dioxide is one of the most widely employed photocatalytic semiconducting materials because of the peculiarities of chemical inertness, non-photocorrosion, low cost and non-toxicity. The photocatalytic process originates from the generation of charge-carriers, electrons (e^-) in the conduction band and holes (h^+) in the valence band, as a result of photoexcitation of semiconductors. The $HO^\bullet$ free radicals, which are recognized as the major oxidant in photocatalytic degradation, are formed by interfacial charge transfer reactions between holes and surface hydroxyl groups or preadsorbed water [5]. On the other hand, the generated holes may recombine with conduction band electrons or get trapped in surface states, lowering significantly quantum efficiency. Therefore, preventing recombination of electrons and holes is crucial to the improvement of the photocatalytic activity of semiconductors. An increase in the charge-carrier lifetime or the interfacial charge transfer rate is expected to raise the quantum efficiency of photocatalysis [6]. Carp et al. [1] cited many references and pointed out that doping semiconductors with various metal ions, composite semiconductors, deposition of noble and group VIII metals, and oxygen reduction catalysts can be employed to enhance photocatalytic efficiency. However, a number of methods, such as impregnation, coprecipitation and sol–gel for preparing photocatalysts and widely varying experimental conditions used for evaluation of photocatalytic activity may lead to controversial influences of modification on photocatalytic systems [7–15]. Iketani et al. [16] cited many reports, and pointed out that some systems demonstrated that metal ion doping could increase photocatalytic activity, whereas others showed detrimental effects. Although a great deal of effort has been devoted to the semiconductor photocatalysis, the detailed mechanism of the modifier reagents affecting photocatalytic

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activity of semiconductors is still not completely clear. Conclusively, the number of reported photocatalysts that are able to decompose pollutants effectively enough for commercial practice with reasonable activity has been quite limited.

Grzechulska et al. [17] added KOH to a slightly crystallized TiO_2 slurry, followed by thermal treatment, and indicated that KOH/TiO_2 can improve the photocatalytic decomposition of oil. However, little attention has been given to the investigation of the influence of KOH on the characterization and photocatalytic activity of TiO_2.

Textile dyeing and printing industries are the major contributors responsible for the pollution of the aquatic ecosystems since a great quantities of dyes are consumed and the efficiency of dyeing process is low [18]. Accordingly, treatment of residual dyes has been an important issue of research. Although textile dyes can be disposed via some physical and chemical processes, these methods are usually incomplete and ineffective. Additionally, biological processes exhibited limited efficiency due to xenobiotic and non-biodegradable characteristics of textile dyes. Furthermore, some physical and chemical treatments of dyes can generate the second pollution resulting from toxic products [19]. Alternatively, photodegradation of dyes has important practical applications since the complete destruction or mineralization of toxic and non-biodegradable compounds to carbon dioxide and inorganic constituents can be accomplished.

In the present work, BRL is employed as a model compound to examine the photocatalytic activity of K^+-doped TiO_2 prepared via a sol–gel procedure and thermal treatment.

2. Experimental

2.1. Materials

Titanium tetraisopropoxide (TTIP, Acros, 98%), anhydrous ethanol (Scharlace, 99.8%), potassium hydroxide (Shimakyu, EP), hydrochloric acid (Ferak, GR), and Everdirect Supra Blue BRL dyes (BRL, with structure similar to blue 201, a gift from Ever Comp.) were all used as received without purification. Deionized water (18.2 MΩ cm) was obtained from a Millipore Milli Q^+ system.

2.2. Preparation of the K^+-doped TiO_2 photocatalysts

The K^+-doped TiO_2 photocatalysts were prepared in a manner similar to that used for sol–gel. Typically, 20 ml of anhydrous ethanol was added to 9 ml of TTIP, and then the prepared solution was stirred at room temperature on a magnetic stirrer for about 30 min in the dark under nitrogen atmosphere (solution A). At the same time, the desired amount of potassium hydroxide was dissolved into 200 ml of water, and then the solution was stirred for 30 min (solution B). Solution A was added drop by drop to solution B under vigorous stirring. The resulting solution was stirred at 323 K for 24 h, and then the samples were removed from the solution by centrifugation. The obtained samples were dried at 373 K for 24 h and pulverized; subsequently, they were calcined at the desired temperature for 3 h in a programmable furnace (NEY, 3-525). Finally, the calcined samples were ground into fine powder. Samples with 4.6, 6.7, 9.0 and 14.3% mole fractions of K^+ were designated as K1, K2, K3 and K4, respectively. For comparison, pure TiO_2 samples were also prepared with the same procedures as described above, except that solution B contained no potassium hydroxide.

2.3. Characterization of the prepared photocatalysts

The crystalline phases of the prepared samples were identified by X-ray diffraction (XRD) using a Rigaku D/Max III.V X-ray diffractometer with Cu Kα radiation. The crystal size was evaluated from the half-height width of the diffraction peaks at $2\theta = 25.4^\circ$ (1 0 1) and 27.6°(1 1 0) for anatase and rutile phases using the Scherrer equation. Raman spectra of the samples were recorded by a Raman spectrometer (Ventuno, Jasco). Field emission scanning electron microscopy (FESEM) was applied to obtain the microstructure of the prepared sample using a JSM-6700F JEOL microscope. Diffuse reflectance spectroscopy (DRS) was applied to study the threshold wavelengths and absorption intensities of the prepared samples using a UV-Vis spectrophotometer, equipped with an integrated sphere assembly. The specific surface area, *t*-plot micropore surface area, *t*-plot external surface area, pore volume and *t*-plot micropore volume of the prepared samples were measured by the BET and BJH methods according to the nitrogen adsorption–desorption at 77 K on a Micromeritics ASAP 2020 apparatus.

2.4. Photocatalytic activity measurement

Photocatalytic activities of the samples were evaluated in terms of the decolorization of BRL dye under UV irradiation. Photocatalytic testing was conducted in a thermostatic cylindrical Pyrex reactor with a capacity of 500 ml operated at 298 K. A 125 W mercury lamp (HPI 125 W, Philips), with a major emission at 365 nm, was used as the light source. At the beginning of a run, the desired amount of photocatalyst and 250 ml BRL solution were fed into the reactor. Agitation was supplied by a magnetic stirrer rotating rapidly enough to put the reaction into the region of a chemical reaction control. The solution pH was adjusted by dilute HCl and NaOH solutions. The resulting solution was then stirred continuously in the dark for 2 h to achieve the adsorption equilibrium of BRL on the catalyst. Then the photocatalytic run was started by illumination from the light source. Samples were periodically taken from the reactor, centrifuged at 6000 rpm for 10 min, and then filtered through a 0.22 μm membrane filter before being subjected to an UV-Vis spectrophotometer (Hitachi, U-3010).

3. Results and discussion

3.1. Characterization of K^+-doped TiO_2

The specific surface area, *t*-plot micropore surface area, *t*-plot external surface area, pore volume, *t*-plot micropore volume and pore size of K1, K4 and pure TiO_2 samples calcined at 673, 823, 973, and 1123 K are summarized in Table 1. It is obvious that BET surface area, pore volume, external surface