



Synthesis and Characterization of Visible-Light Active Nitrogen-Doped TiO₂ Photocatalyst

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Nitrogen-doped titania (N-doped TiO₂) has been synthesized through the hydrolysis of N-substituted titanium isopropoxide precursors followed by annealing treatment in air at desired temperatures. The resulting N-doped TiO₂ were characterized using TGA, XRD, BET, XPS, TEM and UV-VIS spectrophotometer. The XRD result showed that the structure of N-doped TiO₂ was anatase. The crystallite size of N-doped TiO₂ increased with the increase of N/Ti proportion. The pore properties were investigated from nitrogen gas sorption analyzer, showing a mesoporous structure of its N-doped TiO₂ with a high specific surface area and a sharp pore radius distribution. The substitution of oxygen sites with nitrogen atoms in the TiO₂ structure was confirmed by X-ray photoemission spectroscopy (XPS). The doping of nitrogen could extend the absorption edge into the visible-light region led to a clear decrease in the band gap on N-doped TiO₂ (compared to pure titania and Degussa P25). The adsorption capacity and adsorption equilibrium constant were also improved by the doping of nitrogen. Catalytic application on methylene blue photodegradation under visible-light irradiation indicated that N-doped TiO₂ provide better activity comparing to the pure ones.

Key Words: Photocatalyst, Nanosize, Optical absorption.

INTRODUCTION

Photocatalysis has been thought to be a fascinating approach for resolving the embarrassments of energy, environment and resource for several decades^{1,2}. Anatase type TiO₂ semiconductor is very often used photocatalyst for water purification and other environmental problem solutions because of its stability, nontoxicity, a relatively satisfied activity, low cost, high oxidation potential and chemically favourable properties³. However, anatase has a high energy of the band gap ($E_g > 3.2$ eV) and therefore could be excited by UV radiation only ($\lambda < 380$ nm). Therefore, developing a modified visible-light sensitive TiO₂ photocatalyst plays an important role in increasing the utilization rate of solar energy and promoting the application of photocatalysis technology and is the most important and challenging research subject in the photocatalysis field⁴.

Early attempts for shifting of TiO₂ absorption into visible-light region mainly focus on the transition metals doping^{5,6} but shortcomings of metal doped TiO₂ such as thermally instability, its tendency to form charge carrier recombination centers⁷, as well as the expensive ion implantation facilities make metal-doped TiO₂ impractical⁸. Recently, nonmetal-ion-doping has been proposed to be an efficient method for preparation of modified TiO₂.^{9,10} Asahi *et al.*⁹ were successfully

intrigued the interest in the anion doping (such as N, C, S, P and F) of TiO₂. Among these anion dopants, nitrogen seems to be the most effective dopant due to its similar size to oxygen and small ionization energy¹⁰. Therefore, nitrogen doped TiO₂ becomes the most studied material relating to its synthesis, characterization and application.

N-doped TiO₂ has been prepared by hydrolytic process¹¹, mechanochemical technique¹², reactive DC magnetron sputtering^{13,14}, solvothermal process¹⁵, high temperature treatment of TiO₂ under nitrogen atmosphere^{9,16} and sol gel method^{17,18}. However, all these processes either required a special apparatus for synthesis or require tight control of experimental conditions. It seems that the sol gel method is the most successful method to prepare N-doped TiO₂ nanoparticles, because it affords simplicity in controlling the nitrogen doping level and particle size by simple variations in experimental condition, such as hydrolysis rate, pH of the solution and solvent systems¹⁷.

In this paper, we report a one step simple sol gel method to synthesize nanometer-sized visible-light N-doped TiO₂ photocatalyst through the hydrolysis of N-substituted titanium isopropoxide precursors. The elemental nitrogen was derived from dodecylamine. The photocatalytic activity of resulted material was estimated in the system of aqueous solution of methylene blue under visible-light, respectively. The contribution of nitrogen doping into titania to the adsorption