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VISIBLE-LIGHT PHOTOCATALYTIC DEGRADATION OF HERBICIDE MECOPROP IN N-DOPED TiO_2 SUSPENSIONS

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Abstract

In this study, the nitrogen-doped TiO_2 crystalline nanopowder was synthesized by calcination of the hydrolysis product of titanium tetraisopropoxide in ammonia. Obtained nanopowder was characterized by XRD and UV-Vis reflection techniques. The kinetics of visible-light (400-800 nm) photocatalytic degradation of herbicide mecoprop in N-doped TiO_2 nanopowder aqueous suspensions was investigated and compared to results obtained for undoped TiO_2.

Introduction

Among the different approaches to pesticide elimination from wastewaters, heterogeneous photocatalysis using semiconductor particles under band gap irradiation has been frequently investigated [1]. Titanium dioxide is the most effective photocatalyst for mineralization of the chemicals in air and water [2]. From the point of view of solar to chemical energy conversion, however, the band-gap energy of TiO_2 is too large for its spectral response to visible, *i.e.* solar light. For utilizing the solar energy efficiently, development of new materials with visible-light-driven photocatalysis is a vital step. Some approaches for shifting of the absorption edge to lower energy, based on TiO_2 modification have been reported [3]. Among these, the simplest and the most feasible approach seems to be nitrogen-doping *i.e.* doping nitrogen atoms into substitutional sites in the crystal structure of TiO_2 (gaining $TiO_{2-x}N_x$). This paper describes the synthesis, and characterization of N-doped TiO_2 nanopowder. Special attention was paid to visible-light photocatalytic activity of N-doped TiO_2 in comparison to commercial undoped TiO_2 (Degussa P25), in reaction of photocatalytic degradation of herbicide *RS*-2-(4-chloro-*o*-tolyloxy)propionic acid (mecoprop) as a model compound.

Experimental

All chemicals used in the experiments were of the highest possible purity. TiO_2 Degussa P25 was used as an undoped photocatalyst. The X-ray diffraction was carried out on a Philips PW 1710 instrument. The UV/Vis reflection spectra of the catalysts were measured using a spectrophotometer Lambda 35 referenced to $BaSO_4$. Kinetics of the degradation was monitored at 229 nm by a Secomam anthelie Advanced 2 spectrophotometer. Conditions of the photocatalytic experiments were previously described [4]. Irradiation in the visible range (400-800 nm) was performed using a 50 W halogen lamp (Philips). The Vis wavelengths were controlled with a 400 nm cut-off filter.

Nitrogen-doped TiO_2 crystalline nanopowder was synthesized by calcination of the hydrolysis product of titanium tetraisopropoxide in ammonia. Titanium tetraisopropoxide and ammonia were mixed in 1:1 ratio at 0°C with vigorous stirring. White precipitate was formed immediately. After washing with water the precipitate was dried at room temperature and calcinated in air.

Results and Discussion

The XRD measurements of the obtained powder revealed that N-doped TiO_2 was in the anatase crystalline phase. From the obtained diffractogram, we calculated the average crystalline size of 12 nm, using the Scherrer formula.

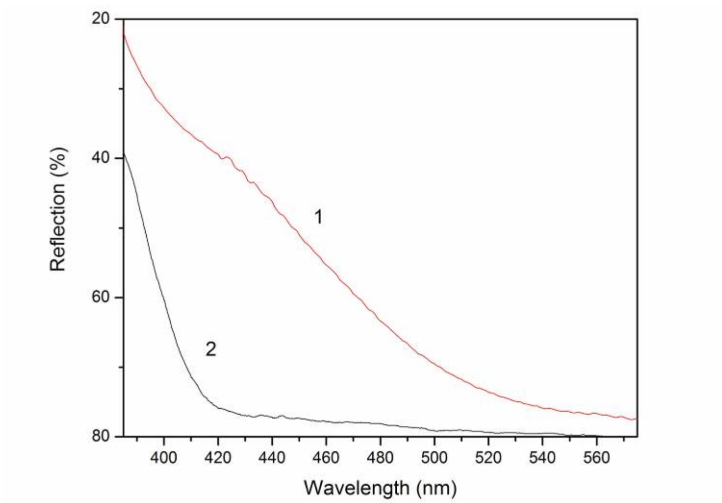

Fig. 1. Reflection spectra of: (1) N-doped TiO_2 nanopowder; (2) TiO_2.

UV/Vis reflection spectra are shown in Fig. 1. It can be seen that nitrogen doping causes the shift of the absorption edge of TiO_2 to lower energy (curve 1) in comparison to undoped TiO_2 (curve 2) from 410 nm to 530 nm.

In order to explore the visible-light photocatalytic activity of TiO_2 and N-doped TiO_2, the degradation of mecoprop in TiO_2 suspensions by visible-light was investigated. Kinetic curves for direct photolysis of mecoprop (curve 1), as well as for photocatalytic degradation in TiO_2 (curve 2) and N-doped TiO_2 (curve 3) suspensions are presented in Fig. 2. Kinetic curves presented in Fig. 2 were obtained by spectrophotometric monitoring of mecoprop degradation. N-doped TiO_2 showed higher visible-light photocatalytic activity (v = 1.36 x 10^{-6} mol dm^{-3} min^{-1}) in comparison to undoped TiO_2 (v = 0.85 x 10^{-6} mol dm^{-3} min^{-1}).

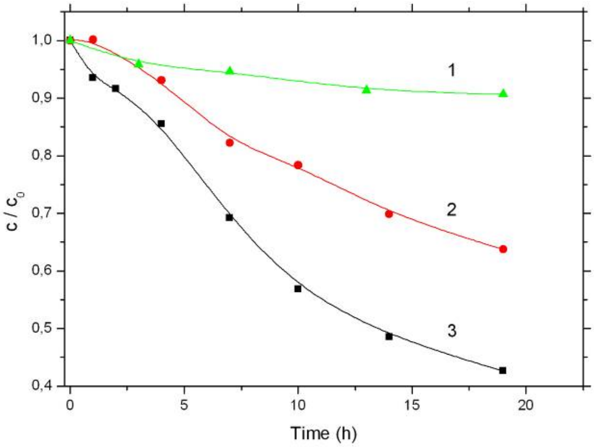

Fig. 2. Kinetics of degradation of mecoprop (2.7x10^{-3} mol dm^{-3}) by using halogen lamp: (1) direct photolysis; (2) TiO_2 (2 mg cm^{-3}); (3) N-doped TiO_2 (2 mg cm^{-3}).

It is considered that nitrogen atoms in doped TiO_2 crystalline nanopowder were responsible for the significant enhancement of its photoactivity under visible light irradiation. However, the obtained visible-light photoactivity of undoped TiO_2 was unexpected. This finding can be explained by the polycrystallinity of TiO_2 Degussa P25: 75% anatase crystalline phase (E_g = 3,2 eV, λ_{edge} = 385 nm) and 25% rutile crystalline phase (E_g = 3,0 eV, λ_{edge} = 410 nm), which enables TiO_2 to absorb a small fraction of visible light (400-800 nm) and subsequently photocatalyse degradation of mecoprop.

Conclusion

The proposed synthetic method resulted in formation of N-doped TiO_2 powder in anatase crystalline phase with particle size ~12 nm. Nitrogen-doping of TiO_2 shifts its absorption edge to lower energy (longer wavelengths ~ 530 nm) in comparison to undoped TiO_2. As a result, visible-light photocatalytic activity of N-doped TiO_2 towards degradation of herbicide mecoprop, was 1.5 times higher than that of undoped TiO_2 (Degussa P25).

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