

Synthesis and investigation of photocatalytic activity nitrogen doped TiO₂ nanotubes

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Abstract

Nitrogen-doped TiO₂ nanotubes (N-TiO₂) were obtained by hydrothermal method at the temperature of 150 °C and a pressure of 0.2 MPa and their structural and physico-chemical characteristics were studied. The source of nitrogen for the modification titanium dioxide nanotubes was urea. To characterize of the obtained photocatalyst the electron microscopy and energy dispersive X-ray spectroscopy (EDX) were used. Investigation of the morphology and structure of N-TiO₂ showed that the powder is a mixture of agglomerated after annealing nanoparticles in the form of flakes and nanowires. The presence of nitrogen in the structure of the modified TiO₂ nitrogen was confirmed using energy dispersive X-ray spectroscopy. The X-ray diffraction pattern of the photocatalyst sample shows that the composition of N-TiO₂ is a mixture of anatase and rutile in a ratio of 60% and 40%, respectively. Modification with nitrogen does not lead to a change in the phase ratio in TiO₂ powder and the change in crystallite size before and after modification. The photocatalytic activity of nitrogen-modified TiO₂ was studied by methyl orange (MO) oxidation. The photocatalytic activity was evaluated from the methyl orange solution absorbance change. As a light source, a fluorescent lamp was used. The concentration of the dye was determined by the spectrophotometric method. The degree of decoloration of the MO solution to N-TiO₂ presence is 10 times higher than for pure titanium dioxide photocatalyst. The increase of photocatalytic activity for nitrogen-modified titanium dioxide is associated with an increase in the specific surface area and, correspondingly, in the yield of hydroxyl radicals formed as a result of the photocatalytic process. The kinetic parameters of photocatalytic oxidation of MO in the presence of N-TiO₂ are calculated. The rate of photocatalytic oxidation of MO at the presence of pure and modified TiO₂ nanotubes was determined. Oxidation of MO in the presence of N-TiO₂ upon irradiation with fluorescent light corresponds to a first-order kinetic equation. The resulting photocatalyst has a higher activity than unmodified TiO₂ nanotubes.

References

- [1] V.K. Ivanov, V.D. Maksimov, A.S. Shaporev, A.E. Baranchikov, B.R. Churagulov, I.A. Zvereva, Yu.D. Tretyakov. Hydrothermal synthesis of effective photocatalysts based on TiO₂. *J. Inorg. Chemistry*. **2010**. Vol.55. No.2. P.184-189. (russian)
- [2] X. Chen, S.S. Mao. Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. *Chem. Rev.* **2007**. Vol.107. No.7. P.2891-2959.
- [3] H. Irie, Y. Watanabe, K. Hashimoto. Carbon-doped Anatase TiO₂ Powders as a Visible-light Sensitive Photocatalyst. *Chem. Lett.* **2003**. Vol.32. No.8. P.772-774.
- [4] S.M. Gupta, M. Tripathi. A review on the synthesis of TiO₂ nanoparticles by solution route. *Cent. Eur. J. Chem.* **2012**. Vol.10. No.2. P.279-294.
- [5] D.P. Macwan, P.N. Dave, Sh. Chaturvedi. A review on nano-TiO₂ sol-gel type syntheses and its applications. *J. Mater. Sci.* **2011**. Vol.46. No.11. P.3669-3686.
- [6] A. Fujishima, T.N. Rao, D.A. Tryk. Titanium dioxide photocatalysis. *J. Photochem. Photobiol. C: Photochem. Rev.* **2000**. Vol.1. No.1. P.1-21.
- [7] X. Chen, S.S. Mao. Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. *Chem. Rev.* **2007**. Vol.107. No.7. P.2891-2959.

- [8] E.A. Kozlova, A.V. Vorontsov. Multiple increase in the photocatalytic activity of TiO₂ by combining the mesoporous structure and platinum nanoparticles. *Russian nanotechnology*. **2007**. Vol.2. No.11-12. P.72-74. (russian)
- [9] D. Zhang. Enhancement of the Photocatalytic Activity of Modified TiO₂ Nanoparticles with Zn²⁺ Correlation between Structure and Properties. *Russ. J. Phys. Chem. A*. **2012**. Vol.86. No.3. P.489-494.
- [10] F.F. Orujov, F.G. Gasanova, Z.M. Aliev, A.B. Isaev, Photoelectrocatalytic oxidation of phenol on platinum-modified TiO₂ nanotubes. *Russian nanotechnology*. **2012**. Vol.7. No.9-10. P.44-47.
- [11] C. McCullagh, N. Skillen, M. Adams, P.K. Robertson. Photocatalytic reactors for environmental remediation: a review. *J. Chem. Technol. Biotechnol.* **2011**. Vol.86. No.8. P.1002-1017.
- [12] J.A. Byrne, P.A. Fernandez-Ibanez, P.S.M. Dunlop, D.M.A. Alrousan, J.W.J. Hamilton. Photocatalytic Enhancement for Solar Disinfection of Water: A Review. *Int. J. Photoenergy*. **2011**. Article ID 798051.
- [13] A.E. Mohamed, S. Rohani. Modified TiO₂ nanotube arrays (TNTAs): progressive strategies towards visible light responsive photoanode, a review. *Energy Environ. Sci.* **2011**. Vol.4. P.1065-1086.
- [14] H. Tada, M. Fujishima, H. Kobayashi. Photodeposition of metal sulfide quantum dots on titanium (IV) dioxide and the applications to solar energy conversion. *Chem. Soc. Rev.* **2011**. Vol.40. P.4232-4243.
- [15] S.G. Kumar, L.G. Devi. Review on Modified TiO₂ Photocatalysis under UV/Visible Light: Selected Results and Related Mechanisms on Interfacial Charge Carrier Transfer Dynamics. *J. Phys. Chem. A*. **2011**. Vol.115. No.46. P.13211-13241.
- [16] S. Sato. Photocatalytic activity of NO_x-doped TiO₂ in the visible light region. *Chem. Phys. Lett.* **1986**. Vol.123. No.1-2. P.126-128.
- [17] S. Sato, R. Nakamura, S. Abe. Visible-light sensitization of TiO₂ photocatalysts by wet-method N-doping. *Appl. Catal. A: General*. **2005**. Vol.284. No.1-2. P.131-137.
- [18] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga. Visible light photocatalysis in N-doped titanium oxides. *Science*. **2001**. Vol.293. P.269-271.
- [19] N. Serpone. Is the Band Gap of Pristine TiO₂ Narrowed by Anion- and Cation-Doping of Titanium Dioxide in Second-Generation Photocatalysts? *J. Phys. Chem. B*. **2006**. Vol.110. No.48. P.24287-24293.
- [20] C. Di Valentin, E. Finazzi, G. Pacchioni, A. Selloni, S. Livraghi, M.C. Paganini, E. Giamello. N-doped TiO₂: Theory and experiment. *Chem. Phys.* **2007**. Vol.339. No.1-3. P.44-56.
- [21] S.U.M. Khan, M. Al-Shahry, W.B. Ingler. Efficient photochemical water splitting by a chemically modified n-TiO₂. *Science*. **2002**. Vol.297. No.5590. P.2243-2245.
- [22] Y. Izumi, T. Itoi, S. Peng, K. Oka, Y.S. Ishibata. Site Structure and Photocatalytic Role of Sulfur or Nitrogen-Doped Titanium Oxide with Uniform Mesopores under Visible Light. *J. Phys. Chem. C*. **2009**. Vol.113. No.16. P.6706-6718.
- [23] J. Zhang, Y. Wu, M. Xing, S.A.K. Leghari, S. Sajjad. Development of modified N doped TiO₂ photocatalyst with metals, nonmetals and metal oxides. *Energy Environ. Sci.* **2010**. Vol.3. No.6. P.715-726.
- [24] A.B. Isaev, Z.M. Aliev, N.K. Adamadzieva, N.A. Alieva, G.A. Magomedova. Photocatalytic oxidation of azo dyes on Fe₂O₃ nanoparticles under oxygen pressure. *Russian nanotechnology*. **2009**. Vol.4. No.7-8. P.109-113. (russian)
- [25] A.B. Isaev, G.A. Magomedova, N.A. Zakargaeva, N.K. Adamadzieva. Effect of oxygen pressure on the photocatalytic oxidation of chrome brown azo dye using TiO₂ as a catalyst. *Kinetics and catalysis*. **2011**. Vol.52. No.2. P.204-208. (russian)
- [26] M. Janus, J. Choina, A.W. Morawski. Azo dyes decomposition on new nitrogen-modified anatase TiO₂ with high adsorptivity. *Journal of hazardous materials*. **2009**. Vol.166. No.1. P.1-5.