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Photocatalytic Degradation of Organic Pollutants by Using Nanocrystalline Boron-doped TiO₂ CatalystsRani P. Barkul,^[a] Radhakrishna S. Sutar,^[a] Meghshyam K. Patil,^[a] and Sagar D. Delekar^{*(b)}

In this work, bare or mixed environmentally non-benign organic pollutants have been decontaminated using boron-doped TiO₂ nanoparticles (B@TiO₂). B@TiO₂ nanoparticles (NPs) with varying content of boron (0.0 to 7.0 mol%) are synthesized using sol-gel method. These NPs are characterized by using different tools. XRD reveals the high crystalline nature with formation of anatase phase and also shows slight increase in crystallite size with increase in boron content in TiO₂ host lattice. The optical shift towards higher wavelength increases with increase of boron doping and hence corresponding

decrease in optical band gap of doped NPs is confirmed. FTIR and TGA studies reveal the increase of surface hydroxylation of NPs with increase in dopant content. B@TiO₂ samples have been used for the photocatalytic degradation of bisphenol A, rhodamine B, methylene blue, methyl orange and mixture of these three dyes under sunlight illumination. 7.0 mol% B@TiO₂ has shown the best activity than other prepared samples. Rate of degradation of mixed dyes using 7.0 mol% B@TiO₂ is about seven times higher to that of bare TiO₂ and also shown higher rate than other doped samples.

Introduction

Environmental concern is become more challenging day-by-day due to increasing human population, rapid increase in industrialization and hence it results various consequences to living beings. Acid rain, ozone depletion, drought zone, heavy rain fall, hurricanes, etc. are the recent environmental crisis observed globally. In addition, the discharge of industrial effluent into the water stream is also very dangerous to human beings. Particularly, in textile industries, industrial effluent containing dyes are coming to the earth system; which gives rise to the air as well as water pollution. These dyes are also often difficult to decompose in water as they have composite molecular structures that cause them to be more stable toward light and resistant to biodegradation.^[1–3] Furthermore, emerging contaminants such as pharmaceuticals, pesticides, industrial chemicals, surfactants, personal care products and endocrine disruptors are also responsible for water pollution, which can cause cancerous tumors, birth defects, other developmental disorders, endocrine disrupting activity and other toxic mechanisms.^[4–6] Tremendous research is devoted on to control the environment pollution especially on degradation of these organic pollutants through different protocols. Some of them are physico-chemical precesses (membrane processes, reverse osmosis, ion exchange, biosorption, activated carbon adsorption, etc.), biological methods (bacterial aerobic and anaerobic biodegradation, fungal degradation, enzymatic degradation,

etc.), advanced oxidation process (photocatalysis, ozonation, UV/ozone, ozone/hydrogen peroxide, Fenton process, photo-Fenton, electrochemical oxidation, etc.) and so on.^[7–10] Due to the certain laggings, the individual physico-chemical process is not suitable option; while tedious protocol, high energy demand, frequent maintenance requirement, etc are shortcomings of the biological methods. Hence, semiconducting photocatalysis based advanced oxidation process having the overriding advantages for photocatalytic transformations. As concerned to the photocatalytic degradation, semiconductor photocatalysis with a primary focus on TiO₂ as a durable photocatalyst has been applied to a variety of problems of environmental interest for water and air purification.^[11] TiO₂ has promoted effective efficiency when activated by UV irradiation ($\lambda \leq 387$ nm). TiO₂ is responsible for the photo-generation of holes (h^+) at the photoanode surface, which can oxidize adsorbed water molecules and/or hydroxyl ions producing hydroxyl radicals ($\cdot OH$).^[12] These radicals are responsible to promote efficient degradation of organic compound as a contaminant present in effluent or dye.^[13–15] However, TiO₂ having UV-driven activity, largely inhibits its overall efficiency under natural sunlight, which consists of less than 5% UV (300–400 nm), and majorly visible (400–700 nm), infrared (700–2500 nm) i.e. 43% and 52% respectively.^[16,17]


Last few decades, several approaches and strategies have been developed to improve the optoelectronic properties of TiO₂ as photocatalyst, which includes doping with metal or non-metals, formation of composite with other materials, photosensitization and so on.^[18–21] On more general grounds, the main purpose of all the studies are to modify TiO₂ to capable it to work in visible light by keeping original network intact.^[22] Modified TiO₂ with doping is one of the effective way to tune the material properties, without disturbing original structure of TiO₂ with a degree of substitution that goes beyond the doping level appears as a challenging and

[a] Dr. R. P. Barkul, R. S. Sutar, Dr. M. K. Patil

Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, Sub-campus Osmanabad, 413 501, MS, India

[b] Prof. S. D. Delekar

Department of Chemistry, Shivaji University, Kolhapur, 416 004, MS, E-mail: sddelekar7@rediffmail.com

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