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Mesoporous nitrogen doped nano titania—A green photocatalyst for the effective reductive cleavage of azoxybenzenes to amines or 2-phenyl indazoles in methanol

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ABSTRACT

A new nitrogen precursor, hydrazine hydrate was used in the synthesis of nano-sized, N-doped TiO_2 photocatalyst by a simple wet impregnation method. This photocatalyst was characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), High resolution transmission electron microscope (HR-TEM), UV–vis diffuses reflectance spectra (DRS), photoluminescence (PL) and X-ray photoelectron spectroscopy (XPS). XRD patterns show that the crystal structure of N-TiO_2 resembles anatase phase of TiO_2. The UV–vis spectra indicate an increase in absorption of visible light when compared to TiO_2. Furthermore XPS analysis reveals the presence of the N atom as O–Ti–N linkage substituting the O atom in the TiO_2 lattice and this causes a decrease in oxygen vacancies. N-TiO_2 nanoparticles were used as a green and recyclable heterogeneous photocatalyst for rapid and efficient reductive cleavage of azoxybenzene into their corresponding amines or 2-phenylindazoles with methanol at room temperature under N_2 atmosphere. Azoxybenzenes in neat methanol afforded anilines, while in aqueous methanol (20% water–80% methanol) they formed corresponding 2-phenyl indazoles. In both reductive cleavages, nano N-TiO_2 is more effective than prepared TiO_2, showing that the nitrogen doping could be an excellent choice to improve the photoactivity of TiO_2.

1. Introduction

Azoxybenzene and its derivatives form an important class of organic materials which are extensively used in textile, printing, leather, papermaking, agrochemical, drug and food industries [1,2]. Due to wide applications, substantial quantities of toxic azo compounds are dumped into environment as industrial wastewaters. Recent research has shown that titanium(IV) oxide (TiO_2) photocatalysts display excellent activity for a number of industrially useful reactions oriented to the synthesis of fine chemicals [3]. Since photocatalytic reaction satisfies several of the requirements for green chemistry [4], organic synthesis of various compounds using photocatalysis has been studied by many researchers [5,6]. Nowadays, environmental pollution and energy crises open up opportunities for novel green photocatalytic routes leading to the modification of TiO_2 to make it solar active, in order to allow the use of sunlight as the energy source of fine chemical production processes. Metal doping has been found to be an efficient approach to enhance visible light absorption [7]. However metal doping causes thermal instability and metal centers act as electron traps, which reduce photocatalytic efficiency [8]. Non-metal doping not only reduces the band gap but also decreases the electron hole recombination leading to higher photocatalytic activity [9]. Among the non-metals, nitrogen doped catalyst is found to be most efficient for the degradation and organic synthesis [10,11].

Shibata et al. reported that photocatalytic processes occurring on suspended TiO_2 powder in methanol solution containing azobenzenes gave rise to 1,2,4-triphenyl-1,2,4-triazolidines or 2-phenylindazoles with low to moderate yield [12]. Although various photocatalytic reactions to yield amines such as reduction of azobenzenes in alcohols [13], reduction of azobenzene to amines by sodium decatungstate–zirconia ($Na_4W_{10}O_{32}/ZrO_2$) nanocomposite [10] and reduction of nitro aromatics were reported [14], no one had studied the conversion of azoxybenzene to either amine or indazoles by N-TiO_2 so far.

In this paper, an attempt has been made for the preparation of N-doped TiO_2 by simple wet method using nano titania obtained from titanyl nitrate and hydrazine hydrate as a nitrogen source. The efficiency of N-TiO_2 photocatalyst has been evaluated by the selective reductive cleavage of azoxybenzene to either aniline derivatives with wide use in the dye, textile, printing, resin, food and pharma industries, or to indazoles with application in pharma industries [15,16]. From the point of view of eco-friendly production of chemicals, attention was paid to the choice of solvent. We used methanol

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