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ORIGINAL ARTICLE

Carbon/nitrogen-doped TiO_2: New synthesis route, characterization and application for phenol degradation

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Abstract Porous nanocrystalline carbon and nitrogen (CN)-doped TiO_2 photocatalyst was prepared using carbon tetrachloride and polyaniline as precursors. The obtained powders were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), Raman spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, and gravimetric analysis. The purpose of this work was to explore the state and location of nitrogen and carbon atoms introduced inside the TiO_2 lattice and to study the exploitation of the photocatalytic activity of the CN-doped TiO_2 for application in phenol degradation under UV illumination. After 30 min from the illumination onset, 64% and 57% of the phenol were degraded when the CN-doped TiO_2 and TiO_2 catalysts were used respectively.

1. Introduction

TiO_2 is one of the commonly used materials in many aspects of life. It is a cheap, harmless, chemically and thermally stable, environmental friendly and nontoxic material. Furthermore, it is considered to be an excellent and promising material in paints (Zhanga et al., 2012), photocatalysis for water splitting (production of hydrogen fuel using solar energy) (Fujishima and Honda, 1972), cosmetics and health care products, degradation of water pollutants, air purification, dye-sensitized solar cell (DSSC) electrodes, sensors and catalysts' support.

Titanium dioxide photocatalytic applications are based on the fact that, in the presence of oxygen and ultraviolet (UV) radiations, it can generate highly reactive oxygen free radicals such as, $HO_2^{\cdot}$, $HO^{\cdot}$ and $O_2^{\cdot-}$ that can oxidize a large number of organic refractory compounds (Shawabkeh et al., 2010). Doping of TiO_2 using metal or non-metal atoms is a promising way to enhance its photocatalytic activity. When an oxygen

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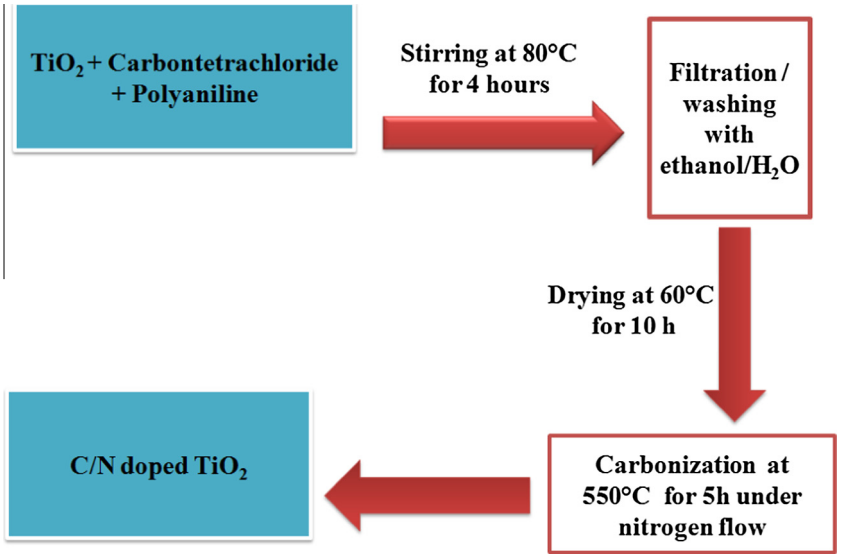

Figure 1 Scheme summarizes the procedure for the C/N-doped TiO_2 preparation.

atom, in TiO_2, is replaced by lighter elements e.g. boron, carbon or nitrogen, the valence band of TiO_2 may be depopulated by three, two or one electron, respectively. At the same time, the introduction of intraband gap states will allow TiO_2 to absorb light in the visible region. It is worthy to mention that the higher the atomic number of the dopant element, the lower is the energy of the corresponding 2p states due to the bigger nuclear effective charge. In fact, it is reported that doping TiO_2 with carbon and nitrogen increases the photocatalytic activity and in turn increases the rate of organic compound degradation (Huang et al., 2008).

Phenolic compounds are considered as one of the most toxic industrial pollutants; they are produced as intermediates in many industries e.g. adhesives and antiseptics (Alnaizy and Akgerman, 2000). So, many works have been done to find an effective way to remove them from wastewater.

Some well-known methods for water treatment e.g. chemical precipitation, ion-exchange adsorption, filtration, and membrane systems are not efficient enough to destroy refractory organic pollutants. Besides, their implementations are limited because of the high cost and the sophisticated equipment they need (Panda et al., 2011). One of the most efficient ways that, recently, started to gain more attention is using heterogeneous semiconducting photocatalysts in an advanced oxidation process (Shu et al., 2010). Advanced oxidation process (AOP) gets rid of phenolic compounds by irradiating them with light in the presence of a suspension of semiconductor metal oxide particles e.g. titanium dioxide and zinc oxide in addition to adding an oxidizing agent e.g. H_2O_2 or ozone. This process involves the generation of reactive hydroxyl free radicals that are potent enough to oxidize many organic pollutants such as phenols. This method is considered to be excellent because of the low-cost, moderate temperature and pressure conditions and it mineralizes completely the pollutants to water, carbon dioxide and mineral acids in short times, (Gupta et al., 2006; Lachheb et al., 2002; Bhatkhande et al., 2002). To increase the efficiency of the AOP, in fact, previous works have been directed for using nitrogen-doped TiO_2 for phenol degradation. For example, Sakthieval et al. used visible light and nitrogen-doped TiO_2 to mineralize 4-chlorophenol. They noticed that doping TiO_2 with nitrogen lowered the TiO_2 band gap energy by 40–80 meV (Sakthivel et al., 2004). 4-Chloro-phenol degradation using TiO_2 with and without Pt nanoparticles was studied also using Neppolian et al. (2007). The nitrogen-doped TiO_2 that Kisch et al. has prepared was used to degrade formic acid and was reported to lower the band gap energy of TiO_2 by 0.07–0.16 eV (Kisch et al., 2007). Venkatachalam et al. used sol gel method to prepare nitrogen-doped TiO_2 and used it for degrading Bis-phenol A using visible light irradiation (Venkatachalam et al., 2006). Instead of the TiO_2 nanoparticles, Dong et al. used nitrogen-doped TiO_2 nanotubes for degradation of methyl orange using visible light. They found a significant increase in the photocatalytic behavior of doped nanotubes compared to the non-doped ones (Dong et al., 2009). Li et al., used activated carbon and nitrogen-doped TiO_2 which has excellent visible photocatalytic activity to remove formaldehyde from air (Li et al., 2010).

The objective of this work was to prepare C/N-doped TiO_2 and use it as a photocatalyst for the degradation of phenol-contaminated water. Although preparing and studying the photocatalytic behavior of C/N-doped TiO_2 toward degradation of many organic compounds is not new but the starting materials that were used in this work are new. In addition the targeted organic compound was phenol which was not previously studied before using C/N-doped TiO_2 using UV irradiation.

2. Experimental

2.1. Materials

Titanium dioxide (anatase 99%) was purchased from Nanostructured & Amorphous Materials, Inc. USA. Aniline, dimethyl sulfoxide, ammonium peroxydisulfate, and ammonia solution were purchased from Sigma Aldrich, Germany. For carbon tetrachloride, it was obtained from BDH Middle East LLC.