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Hydrothermal synthesis of photoactive nitrogen- and boron- codoped TiO_2 nanoparticles for the treatment of bisphenol A in wastewater: Synthesis, photocatalytic activity, degradation byproducts and reaction pathways

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ABSTRACT

Hydrothermal technique was employed for the synthesis of N- and B-codoped TiO_2 at different atomic percentages and calcination temperatures (350 and 400 °C). Borane *tert*-butylamine complex was used as a novel precursor for the dopant atoms. The photocatalytic activities of catalysts were evaluated for destruction of bisphenol A (BPA) spiked in clean water and in secondary treated wastewater influent (SWI) collected from the Groundwater Replenishment System GWRS (Orange County, CA, USA), the world's largest water purification system for indirect potable reuse. Results of X-ray photoelectron spectroscopy (XPS) revealed the incorporation of N and B atoms onto TiO_2 lattice via substitution of O and/or Ti, and interstitial incorporation mechanisms. Carbon doping (graphite-like carbon; O-C = O) was also evidenced from XPS spectra. X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HR-TEM) revealed pristine TiO_2 and all doped TiO_2 existed in anatase structure. The anatase phase of catalysts was further confirmed by simulation of selected area electron diffraction (SAED) of the catalysts and reported anatase TiO_2 using the simulation software CrysTBox (v 1.10). Among all prepared catalysts, 2.0NBT-350 (N + B = 2.0%, calcination = 350 °C) possessed the smallest particle size (12.9 nm), largest BET surface area (108.5 m^2/g) and highest visible-light absorption (i.e., $\lambda > 400$ nm). Simulated solar light/2.0NBT-350 system exhibited the maximum removal of BPA (0.1 μM) at the optimum catalyst dose of 0.8 g/L in clean water, over three consecutive degradation reuse cycles without any noticeable decrease in its photocatalytic activity. BPA was also successfully removed in SWI water, however with slower kinetics due to hydroxyl radical quenching effect of dissolved organic and inorganic species present in the SWI matrix. Degradation byproducts were identified by LC/Q-TOF-ESI-MS analysis. Six byproducts were found in the reaction mixture, with two compounds were newly identified in the current study. BPA oxidation routes comprised successive BPA hydroxylation, elimination of aromatic ring, ring opening, and cyclization of aliphatic compounds. This study is a promising demonstration for controlled design and synthesis of photocatalysts useful for environmental applications, especially for the treatment of BPA in wastewater effluents.

1. Introduction

Titanium dioxide (TiO_2) has been widely recognized as an environmentally friendly, easy to prepare, stable, and cheap catalyst with light activity, mainly in the UV region. These characteristics were the driving force for the extensive use of TiO_2 material in various fields including dye-sensitized solar cells, photocatalytic hydrogen production, and in environmental remediation purposes such as water treatment [1–8]. TiO_2-based AOPs showed capacity to destroy several environmentally recalcitrant pollutants such as humic acids, polysaccharides and conjugated aromatic compounds found in water [9]. However, the weak visible light absorbance has been one of the

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