



Preparation and characterization of TiO₂-based nanosheets for photocatalytic degradation of acetylsalicylic acid: Influence of calcination temperature



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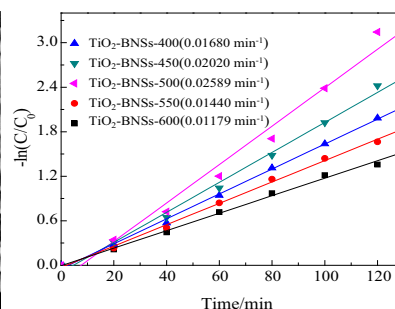
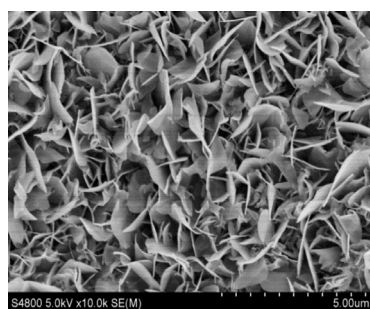
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HIGHLIGHTS

- TiO₂-BNSs were synthesized by hydrothermal method on the surface of Ti plates.
- Calcination temperature affected the architecture and crystal property of BNSs.
- TiO₂-BNSs-500 showed high anatase crystallinity and highly ordered structure.
- TiO₂-BNSs-500 displayed high separation and transfer of the photoinduced electrons.
- TiO₂-BNSs-500 exhibited excellent photocatalytic efficiency.

GRAPHICAL ABSTRACT



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ABSTRACT

TiO₂-based nanosheets (BNSs) were synthesized via hydrothermal method and acid-washing procedure, followed by calcinating at different temperatures in air. The resulting TiO₂-BNSs were characterized by XRD, SEM, DRS and PL. The photoelectrochemical properties of TiO₂-BNSs were measured through transient photocurrent response (TPR), open-circuit potential (OCP) and electrochemical impedance spectroscopy (EIS). The prepared TiO₂-BNSs were used to the photocatalytic degradation of acetylsalicylic acid. The results indicated that the samples calcinated at different temperatures exhibited the nanosheets architectures with the lengths in the range of 500–1500 nm and thickness of approximately 30 nm. The crystallinity of the samples enhanced as increasing the calcination temperature from 400 °C to 600 °C. Among the TiO₂-BNSs samples, the 500 °C-calcinated nanosheets (TiO₂-BNSs-500) exhibited the relatively uniform and regular nanosheet structure. The phase transformation from anatase to rutile phase happened at 500 °C. TiO₂-BNSs-500, TiO₂-BNSs-550 and TiO₂-BNSs-600 possessed the biphasic structure of anatase-rutile. And, the visible light absorption, electron–hole pairs separation and transfer efficiency, photocatalytic activities for the degradation of acetylsalicylic acid and ·OH yield of the samples presented the similar variation tendency which improved as increasing the calcinated temperatures from 400 to 500 °C and then declined at 550 and 600 °C. Accordingly, the degradation rate of acetylsalicylic acid for 120 min reaction was 87.8% when TiO₂-BNSs-500 was employed as the photocatalyst. The photocatalytic degradation reaction fitted the pseudo-first-order kinetics and ·OH was the crucial oxidative species.

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1. Introduction

Photocatalytic oxidation technology has been regarded as an effective, environmentally friendly and promising means in wastewater remediation applications [1,2]. Up to now, a wide selection of semiconductors were used as the photocatalysts such as TiO_2 [3], V_2O_5 [4], CeO_2 [5], $g\text{-C}_3\text{N}_4$ [5], Ag_3PO_4 [6] and so on [2,4,6]. Notably, over the past several decades, studies of using TiO_2 as a photocatalyst in wastewater treatment has been widely investigated and TiO_2 is still the most popular photocatalytic material owing to its intrinsic attributes, including the high photoreactivity, non-toxicity, low cost, superior oxidizability and long-lived (around 250 ns) charge carriers [7–11]. Generally, TiO_2 exists in three most commonly polymorphs: brookite, anatase and rutile [12]. Among the three polymorphs only brookite has not been employed as the photocatalyst because of its metastable structure [13]. As demonstrated, the pure anatase shows the higher photoreactivity than the single rutile structure. The poor photocatalytic activity of the rutile is mainly attributed to its higher recombination rate of the photoinduced electron–hole pairs and the greater crystallite size, which can be transformed from brookite and anatase when increasing the calcination temperatures [14,15]. Furthermore, a biphasic anatase–rutile TiO_2 with a singularly high photocatalytic performance can be obtained by controlling the calcinating temperature. It is thought that the higher electron–hole separation efficiency and the excellent crystallinity are favorable for the expanded photocatalytic property of TiO_2 [16]. Moreover, the change in the surface morphology has a direct influence on the light absorption and the photoinduced electrons separation and transfer characteristics of TiO_2 [17,18].

Compared with the traditional pulverous TiO_2 catalyst, the TiO_2 nanomaterials immobilized on the Ti substrates can avoid the photocatalyst runoff and the secondary pollution because TiO_2 -based nanomaterials can effectively be separated and recycled from a slurry system in practical applications. The TiO_2 nanomaterials prepared in-situ on the Ti substrates through the electrochemical anodic oxidation [17] or hydrothermal method [19] has been attracting considerable attention due to the stronger junctions between TiO_2 and Ti substrate and the simple operation relative to other methods such as the sol–gel followed by coating [20], vacuum sputtering [21] and chemical vapor deposition [22]. TiO_2 -based nanotubes film conducted by the anodization have been reported by many researchers [17,23,24]. The hydrothermal method has been also used for designing and preparing various TiO_2 -based nanomaterials, e.g., hierarchical TiO_2 -based nanowires [19], layered TiO_2 -based nanosheets (BNSs) [25] and rutile TiO_2 -based hollow nanorods [26], wherein the advantages of the hydrothermal procedure is facile, perfect dispersibility, small particle size and environmentally friendly. In addition, this preparation method can be easily extended to change the element component of the thin films on the surface of TiO_2 -based nanomaterials [25,27–29].

It is well documented that the physical and chemical performances of TiO_2 -based nanomaterials were strongly dependent on the fabricating conditions. With the variation of operational parameters, the controllable preparation of TiO_2 -BNSs with some surface microstructure, grain size and form and photocatalytic activities of TiO_2 -BNSs were reported. Usually, the hydrothermal temperature, the reaction time, the concentration of the reactants and pH of the solution [30,31] were studied. However, the results showed that the subsequent calcination treatment had a crucial influence on the surface morphology, crystallite size, crystallinity, phase composition and photocatalytic properties of TiO_2 -based nanomaterials [32,33]. Unfortunately, it was still lack of comprehensive investigation focused on the effect of the calcination temperature on the crystal, optical and photoelectrochemical properties of TiO_2 -based

nanosheets and the photocatalytic degradation of the pharmaceutical wastewater. Typically, the non-steroidal anti-inflammatory drug and their metabolites can be detected in the surface waters, groundwater and drinkable water in the range of ng L^{-1} – $\mu\text{g L}^{-1}$ due to its widespread usage and the incomplete removal of some of these pollutants during the conventional wastewater treatment. The accumulation of non-steroidal anti-inflammatory drug in the environment can cause potential risk to human and animal health by drinking water or food chain [34]. Acetylsalicylic acid belongs to the non-steroidal anti-inflammatory drug groups and it has been used more than 100 years as the antipyretic, analgesic, anti-arthritis and anti-rheumatic drugs.

In this work, TiO_2 -BNSs were prepared through a hydrothermal procedure in a sodium hydroxide aqueous solution with the pure Ti plate as TiO_2 precursors, followed by acid-washing and then calcinated at various temperatures. The morphologies and various crystal properties of the resulting TiO_2 -BNSs were characterized. The optical and the photoelectrochemical performances were studied. And acetylsalicylic acid was selected as the simulate contaminant to evaluate the photocatalytic activity of as-prepared TiO_2 -BNSs and the relevant degradation rate constant were obtained. The influence of the calcination temperature on TiO_2 -based nanosheets and the degradation of acetylsalicylic acid were discussed in details.

2. Experimental

2.1. Preparation of TiO_2 -BNSs

TiO_2 -BNSs were in situ grown by the hydrothermal method in 1 M NaOH aqueous solution with Ti plate as the TiO_2 precursor. The cleaning process of the Ti foils was according to our previous studies [35]. In detail, the cleaned Ti foils were transferred into a stainless para-polyphenyl (PPL)-lined autoclaves of 50 mL inner volume, which were filled with 20 mL of 1 M NaOH aqueous solution. The sealed autoclave was put in an electric oven at 170 °C for 28 h, and naturally cooling down to the room temperature. After the hydrothermal processing, the samples were washed with deionized water for several times and immersed into 0.1 M hydrochloric acid for 24 h by exchanging Na^+ with H^+ . After the immersion in hydrochloric acid, the as-prepared TiO_2 -BNSs were washed with deionized water for several times, and dried at room temperature. The as-prepared samples were calcinated in air at 400, 450, 500, 550 and 600 °C for 2 h with a heating rate of 3°Cmin^{-1} , which were denoted as TiO_2 -BNSs-400, TiO_2 -BNSs-450, TiO_2 -BNSs-500, TiO_2 -BNSs-550 and TiO_2 -BNSs-600, respectively.

2.2. Characterization

X-ray diffraction (XRD) patterns were performed on a Bruker D8 Advance X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($k = 0.15418 \text{ nm}$) to determine the identity of crystalline phase and crystallite size of samples. The accelerating voltage and applied current were held at 40 kV and 30 mA, respectively. The morphology of the as-prepared samples was observed by using a field emission scanning electron microscope (FE-SEM, Hitachi S-4800), using a 5 kV accelerating voltage. UV-visible diffuse reflectance spectra of samples were obtained by using a TU-1901 spectrophotometer, in which BaSO_4 was used as a reference standard. Photoluminescence (PL) spectra were measured on an FP-6500 fluorescence spectrophotometer with the excitation wavelength of 315 nm.

The transient photocurrent response and open-circuit potential of the as-prepared samples were measured on a LK3200 electrochemical workstation in a standard three-cell configuration in

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