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Electro-catalytic characterization and dye degradation of $Ti_{1-x}(Bi)_xO_2$ in acidic solution

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Abstract

The authors in this study used the sol–gel process to prepare Bi-doped TiO_2 as a novel electrocatalyst. Results show that Bi can be doped successfully into TiO_2 from 1% to 90%. The electrical conductivity of a 1% Bi-doped TiO_2 particle-suspended solution is increased nearly twice that of pure TiO_2. The electro-catalyzing property of the synthesized Bi-doped TiO_2 catalyst was performed under acidic conditions toward a methyl blue dye solution. The observed removal percentage of methyl blue dye was from 5% to 75%. The optimized electro-catalyzing condition was observed at 5% Bi-doped TiO_2 with a working voltage of 5 V.

Keywords: A. Sol–gel process; C. Electrical conductivity; D. TiO_2

1. Introduction

Among the most thoroughly studied photocatalysts, such as TiO_2, ZnO, CdS, and ZnS, TiO_2 is the most widely used. It is able to change the excitation energy of pure TiO_2 through doping heteroatoms, for example Bi [1], Eu [2], and IO_3 [3]. In our previous study, we used a nano-sized TiO_2 to remove the styrene monomer from waste gas [4], and the spent solid absorbent could be recycled as (PS)-TiO_2 nano-composite directly.

The disadvantage of using TiO_2 as a photocatalyst is that it must be initiated by photons rather than electrons. Preparing a novel TiO_2-based electrocatalyst requires driving the electro-catalyzing oxidation for toxics in environment. Recently, several studies have found that CNTs, Au, and W can improve the electro-conductivity of TiO_2 [5–7] and ZnO [8]. Hoffman and Xu have proposed a novel Bi-doped TiO_2 with a photoelectro property [1,9,10]. In addition, Kondarides and Lianos reported using a binary photocatalyst alloy with a photoelectrocatalysis property [11]. However, few previous studies have reported how to synthesize the novel Bi doped TiO_2 electrocatalyst.

The sol–gel process is a highly useful method for preparing inorganic compounds with doping [1,12,13]. The authors in this study prepared a Bi-doped TiO_2 electrocatalyst using sol–gel growth to attempt to control the doping amount of Bi. In addition, the pH of a natural water body sample or industrial wastewater is nearly acidic. No study has performed the electro-catalyzing behavior of a synthesized Bi-doped TiO_2 catalyst under acidic conditions. Therefore, the authors performed the electro-catalyzing behavior of a synthesized Bi-doped TiO_2 catalyst under acidic conditions toward a commonly used methyl blue dye solution.

2. Materials

The authors in this study used a sol–gel process to prepare a Bi-doped TiO_2 electrocatalyst. The preparation procedure was a modification of the works of Hoffman and Xu [1,9]. $TiCl_4$ and $BiCl_3$ were purchased from Aldrich chemical company and were used directly without any purification. Due to that $TiCl_4$ and $BiCl_3$ are both hydroscopic and air-sensitive, the reacted gas with air is HCl and is hazardous for experimental operators. Therefore $TiCl_4$ and $BiCl_3$ must be placed and sampled in a dry environment (for example in a big plastic bag under nitrogen gas purging). For each sample, the cover powder must be removed and sample the deeper sample must be used to maintain the purity of the $TiCl_4$ and $BiCl_3$. After mixing, different amounts

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Table 1
The added amount of acetic acid and applied voltage for electronic degradation test.

Parameter	Glacial acetic acid (mL)	Import current (V)
A	0.5	5.0
B	1.0	
C	0.5	10.0
D	1.0	

of the Ti and Bi chloride powder mixture was dissolved in a water–methanol solution (the mixing ratio was 3:1). A 17 N ammonia solution was added into the Ti and Bi containing a water–methanol solution to form a Bi–Ti hydroxide gel, until the white precipitation stops forming. The gel was collected and placed on a glass disc. Methanol was then evaporated from the gel into a hood in air at room temperature before the gel was sintered at 400 °C for 1 h. The synthesized Bi-doped TiO_2 electrocatalyst was milled and stored in a dark environment. The doped amount of Bi into the TiO_2 was controlled at 0.1–90 wt%, based on the mixing ratio of the Ti/Bi chlorides. In the electro-catalyzing oxidation property test, a simple electrolysis cell was composed using 100 mL glass beaker as a reactor and two stainless steel sheets with a thickness of 0.1 cm, a length of 10 cm and a width of 1 cm were used as electrodes. Then 100 mL of a 10 mg/L methylene blue dye solution was added in the reactor with a various weight of the synthesized photocatalyst. The pH of the methylene blue dye solution was controlled by adding 0.5 or 1.0 mL of acetic acid. Furthermore, the working voltage for electro-catalyzing oxidation of the methylene blue dye solution was set at 5.0 V and 10.0 V. The concentration of methylene blue dye solution was performed using a UV spectrometer during the testing period of 0–240 min. Table 1 summarizes the detailed parameters.

The water conductivities that suspends synthesized the Bi-doped TiO_2 electrocatalysts were performed using a commercialized electro-conductivity meter (Gwinstek Co. GPC 3030D).

3. Results and discussion

3.1. Characterizing the synthesized catalyst

The water conductivity that suspends synthesized the Bi-doped TiO_2 electrocatalyst was performed (Fig. 1), the

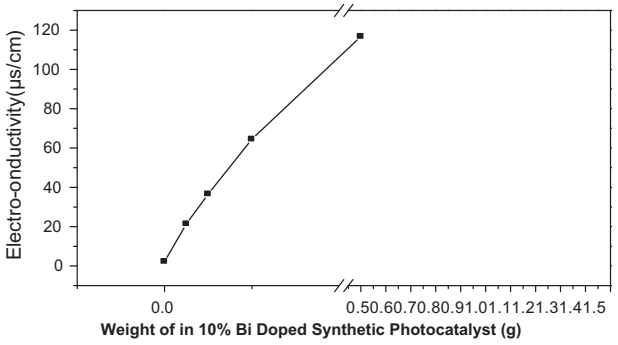

Fig. 1. Conductivity of synthesized 10% Bi doped TiO_2 catalyst in 100 mL water with various gram levels.

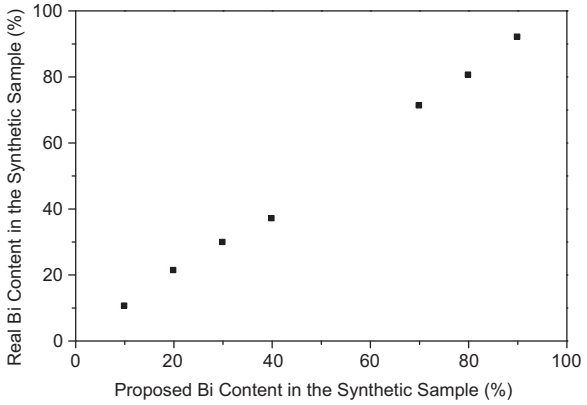

Fig. 2. Relationship between the proposed Bi content and the EDX detected Bi content in the synthetic photocatalyst.

electro-conductivity of pure water is increased when the mixing grams of synthesized a 0.1% Bi-doped TiO_2 electro-catalyst are increased. Results show that the electro-conductivity of a 1% Bi-doped TiO_2 is increased almost two times than pure that of TiO_2. The SEM-EDX was performed on the synthesized Bi-doped TiO_2 electrocatalyst to ensure the doped content of Bi ions in the synthesized Bi doped electrocatalyst. Results show that the calculated Bi content has a linear relationship with the EDX-detected Bi content (Fig. 2). Therefore, the authors successfully synthesized the Bi-doped TiO_2 electrocatalyst using the sol–gel process.

3.2. Assessing the efficiency of electro-catalyzing of dye in an acidic solution

Hoffman and Xu have reported on an electro-catalyzing experiment of Bi-doped TiO_2 [1,9,10], and the buffer solution used in these studies was a NaCl neutral solution. However, in applying this novel Bi-doped TiO_2 electrocatalyst on waste-water is almost under acidic condition. Therefore, we used acetic acid as a buffer solution in the following electrocatalysis test of methyl blue dye.

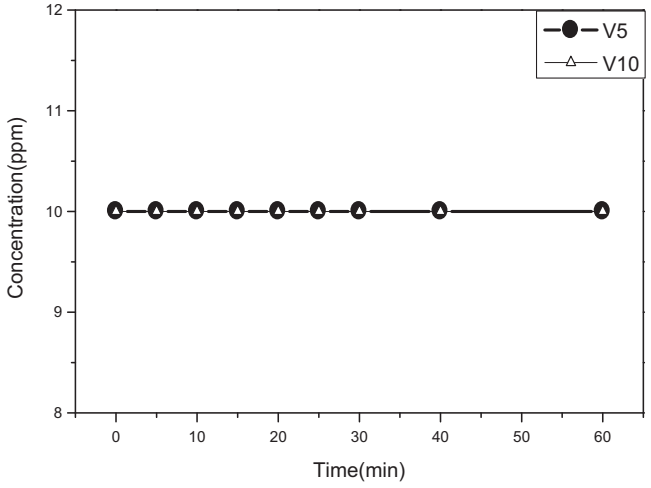

Fig. 3. Electro-degradation of methylene blue in glacial acetic acid by import current 5.0 V and 10.0 V.

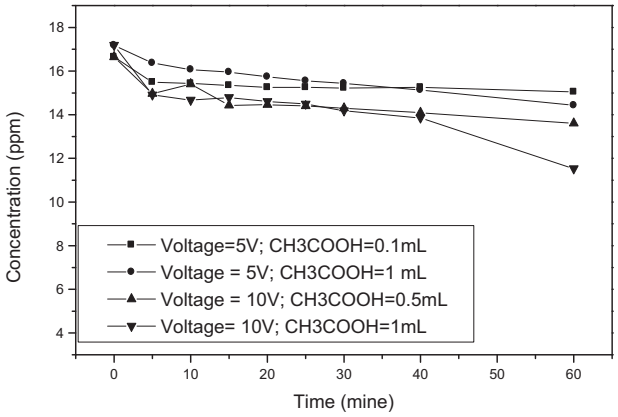

Fig. 4. Electro-degradation of methylene blue by using different parameters without electro-catalyst.

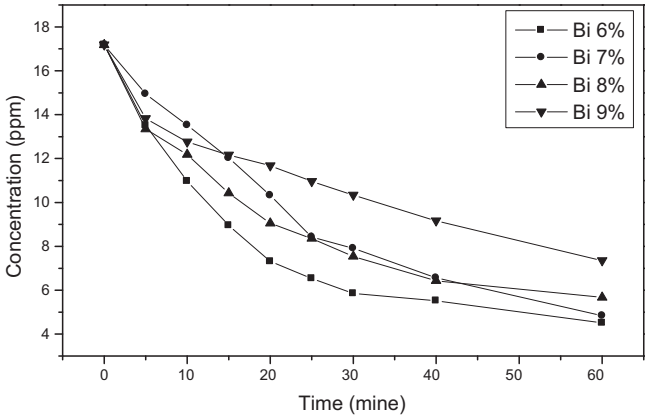

Fig. 6. Electro-degradation of methylene blue b y using synthesized 6–9% Bi doped TiO_2 electro-catalyst.

Figs. 3–6 show the electro-catalyzing oxidation curves of a methylene blue dye solution using various Bi-doped TiO_2 electrocatalysts. Fig. 4 indicates that electro-catalyzing oxidation of a methylene blue dye solution did not occur without any catalyst application. The efficiency estimates of using different acetic acid additions and applied voltages without using any Bi-doped TiO_2 electrocatalyst application are displayed in Fig. 4. The data show that the removal efficiency is observed from 6% to 32%, the ultimized condition is observed at 1 mL acetic acid and 5 V for 60 min, and the methylene blue concentration is reduced from 17.0 mg/L to 11.5 mg/L. Therefore, the authors used the same condition in the following test, as shown in Figs. 5 and 6.

Results in Figs. 5 and 6 show that the removal percentages of the methylene blue dye solution are 71%, 63%, 75%, and 56% when using the pure TiO_2, 3.0% Bi doped TiO_2 electrocatalyst, 5.0% Bi-doped TiO_2 photo-catalyst, and 9.0% Bi-doped TiO_2 photo-catalyst, respectively. Therefore, the authors determined that the optimal Bi-doping amount is 5.0%. For the first time, a synthesized pure TiO_2 catalyst has a 71% removal percentage under acidic conditions.

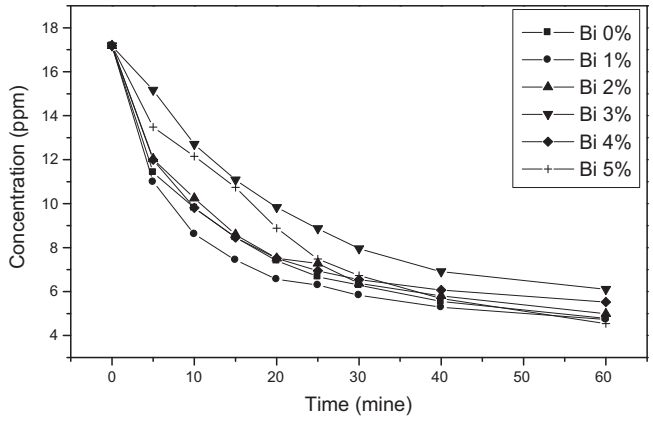

Fig. 5. Electro-degradation of methylene blue by using synthesized 0–5% Bi doped TiO_2 electro-catalyst.

4. Conclusions

The authors in this study successfully synthesized a Bi-doped TiO_2 electrocatalyst using a sol–gel process. These synthesized TiO_2 electrocatalyst could be initiated the electro-catalyzing oxidation toward an acidic methylene blue dye solution by applying a 5-V working voltage. In the future, this novel Bi doped TiO_2 electrocatalyst could be used to manufacture air pollution control devices and control water pollution control.

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