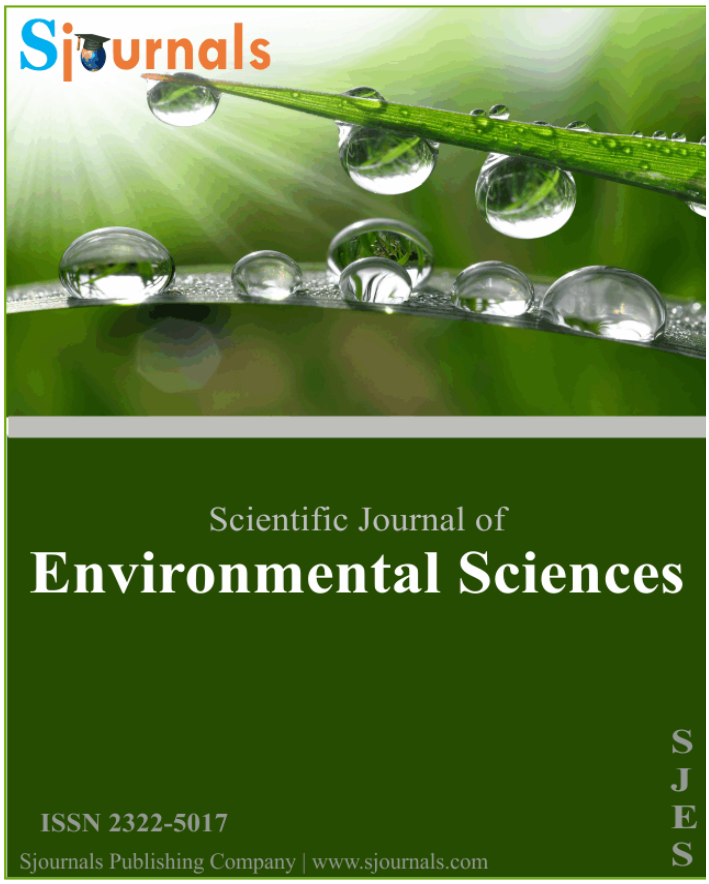

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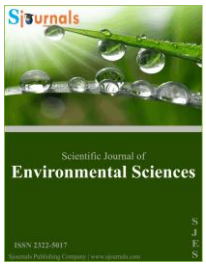

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Original article

Preparation of Bi_2O_3/TiO_2 fixed photocatalysts and degradation of aqueous Bisphenol A under simulated sunlight

Chao-Yin Kuo, Tzu-Hsuan Li, Siang-En Syu*
Department of Safety Health and Environmental Engineering, National Yunlin University of Science and Technology, 123 University Rd., Sec. 3, Douliou, Yunlin 640, Taiwan.

*Corresponding author; Department of Safety Health and Environmental Engineering, National Yunlin University of Science and Technology, 123 University Rd., Sec. 3, Douliou, Yunlin 640, Taiwan.

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ABSTRACT

A series of Bi_2O_3/TiO_2 composite photocatalysts (T, 0.5BT, 1.0BT, 2.0BT, 4.0BT, 6.0BT and 8.0BT) were synthesized and used to degrade aqueous bisphenol A (BPA) under simulated sunlight irradiation. The structures of the photocatalysts were extensively characterized using X-ray diffraction (XRD) and UV-visible diffuse reflectance spectroscopy (UV-vis DRS). UV-visible spectral analysis indicated that all of the Bi_2O_3/TiO_2 photocatalysts shifted their absorption band toward visible light, and reduced energy gap. The experimental results indicated that aqueous BPA with a Bi-Ti atomic ratio of 4:96 was the most effective in degrading BPA under simulated sunlight irradiation.

1. Introduction

The titanium dioxide (TiO_2) photocatalyst has been extensively studied for use in eliminating organic compounds owing to its high activity, chemical stability, nontoxicity, photostability, and low cost (Zhang et al., 2015; Dai et al., 2015; Li et al., 2012; Rauf et al., 2009; Gao et al., 2010). However, since the photoactivity of TiO_2 materials is limited by the wide band gap of pristine TiO_2 (3.2eV), TiO_2 can only absorb UV light with a wavelength of under 387 nm, which represents only occupies about 3-5% of sunlight, limiting its photocatalytic ability in

sunlight (Bettinelli et al., 2007; Xing et al., 2009; Kuo et al., 2010). The relevant literature reveals that the metal doping or nonmetaldoping of photocatalyst shifts their photoresponse from UV to the visible region, extending the photocatalytic activity of TiO_2 toward visible light (Guo et al., 2012; Yu et al., 2011). In this work, bismuth oxide (Bi_2O_3) is doped into TiO_2 to increase its photocatalytic activity, and the combination of these two semiconductor materials effectively reduces the energy gap and the recombination rate of electron hole pairs, and increasing its activity in the visible region (Huang et al., 2009; Lin et al., 2014). The photocatalytic activity of modified catalyst was evaluated in the degradation of bisphenol A (BPA) under simulated sunlight irradiation.

The objectives of this work are to compare the photocatalytic activities of various as-prepared Bi_2O_3/TiO_2 photocatalysts in the removal of BPA under simulated sunlight irradiation, and to measure the wavelengths of light that is absorbed by the prepared photocatalysts.

2. Materials and methods

The photocatalyst P25 TiO_2 (which is a mixture of anatase and rutile forms of titanium dioxide in the ratio 75:25) was obtained from Degussa. Bismuth oxide was obtained from a chemical company in Taiwan. The parent compound, BPA, was purchased from Sigma-Aldrich (purity > 97%). All chemicals were of analytical reagent grade and used as received. Bi_2O_3/TiO_2 fixed photocatalysts were synthesized from TiO_2 and Bi_2O_3 in various mole ratios (Bi:Ti = 0%, 0.5%, 1.0%, 2.0%, 4.0%, 6.0%, and 8.0%). The samples thus obtained were denoted as 0.5BT, 1.0BT, 2.0BT 4.0BT, 6.0BT, and 8.0BT, respectively. Degussa P25, without added bismuth oxide, is denoted as T. The mixture was squeezed into strips by a granulator, and was dried at 105°C for two hours and then calcined at 450 °C for four hours.

The crystalline phases and the absorption wavelengths of the prepared photocatalysts were obtained by X-ray diffraction (XRD) and UV-vis spectroscopy, respectively. The crystallinity of each photocatalyst was analyzed using X-ray diffraction (XRD) using CuKα radiation (Bruker AXS). UV-vis spectroscopy (Jasco V-670) was utilized to profile the absorbance spectra of the photocatalysts at wavelengths of 200-800 nm, from which the photocatalyst band gap energy was calculated. The photocatalytic activity of various photocatalysts was evaluated by using them to degrade BPA solution in a photocatalytic reactor, which consisted of four 30 cm-long quartz tubes. Each tube was filled with 8 g Bi_2O_3/TiO_2 photocatalyst, before 20 mg/L BPA solution was introduced into it using a peristaltic pump. The flow rate of the BPA was 3.6 mL/min. The light source in the column photo-reactor provided 500 W simulated sunlight.

3. Results

3.1. XRD patterns analysis of catalyst

Figure 1 presents the XRD patterns of various prepared photocatalysts. The scanned 2θ range was from 20° to 80°, and the two dominant crystalline structures of photocatalyst P25 TiO_2 were anatase and rutile (Jing et al., 2009). The peaks, associated with diffractions of various crystal planes of anatase, were at the following angles: 25.3°, 36.7°, 37.8°, 38.6°, 48.0°, 53.9°, 55.1°, 62.7° and 75°(JCPDS no. 21-1272). Diffraction peaks at 27.4°, 36.1°, 41.2°, 44.1°, 54.3°, 56.7°, 62.7°, 64.0°, 68.9°and 69.8°, were assigned to other crystal phases of rutile(JCPDS no. 21-1276). The diffraction peaks associated with various crystal planes of bismuth oxide were27.4°, 33.3°and 46.3°. Figure 1 demonstrates that all Bi_2O_3/TiO_2 catalystsincluded both anatase and rutile crystals and the intensity of the characteristic peak at 27.4°increasedwith the relative amount of bismuth oxide. No other crystalline phase of an impurity was observed, and experimental results indicated that the temperature of calcination of the catalyst was 450 °C, as a result of the mixing of bismuth oxide and titanium dioxide.

3.2. UV-Vis spectra analysis of catalyst

Figure 2 plots the optical absorption characteristics of various photocatalysts with mole ratios (Bi/Ti = 0%, 0.5%, 1%, 2%, 4%, 6%, 8%) following calcination at 450 °C. Table 1 presents the band gaps of the photocatalysts, calculated using the equation $Eg = 1239.8/\lambda$, where Eg is the band-gap energy and λ is the absorption wavelength. From Figure 2 and Table 1 observed that band gaps of all Bi_2O_3/TiO_2 photocatalystswere red-shifted toward visible light. There are two different absorption wavelengths of 2.0BT, 4.0BT, 6.0BT and 8.0BT. The second absorption wavelengths were in the visible light region. 0.5BT and 1.0BT couldn't obtain due to fewer amount of bismuth

oxide doped. The red shift was attributed to the doping with bismuth oxide, and the lowering of the band-gap energy of the samples reduced their required driving force, improving their photocatalytic sensitivity (Jalalah et al., 2015).

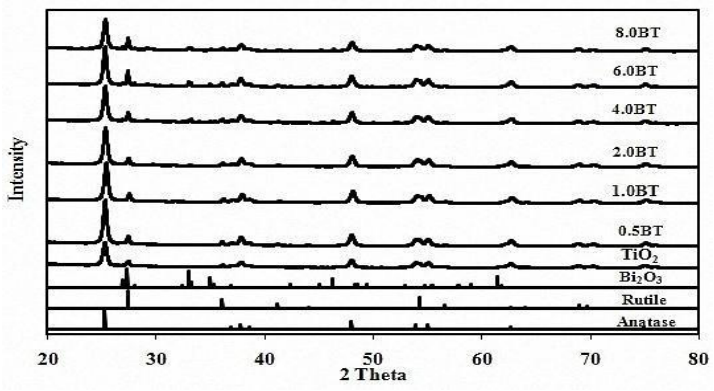

Fig. 1. XRD patterns of various photocatalysts.

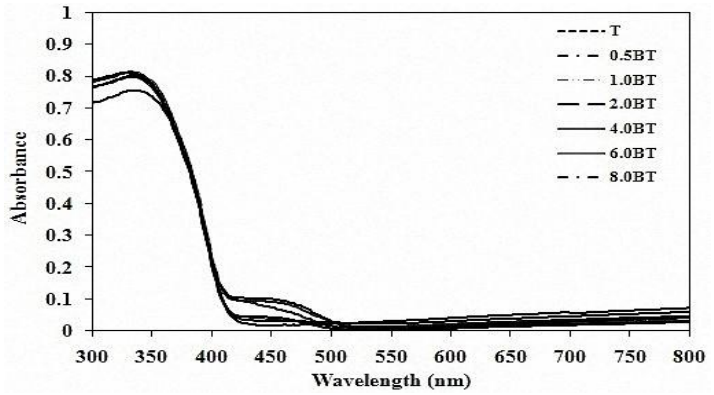

Fig. 2. UV-Vis absorption spectra of various photocatalysts.

Table 1
The absorption wavelength and the energy gap calculation of various photocatalysts.

Samples	Absorption wavelength (nm)	Band gapenergy (eV)
T	412	3.01
0.5BT	415	2.99
1.0BT	415	2.99
2.0BT	416, 506	2.98, 2.45
4.0BT	416, 516	2.98, 2.40
6.0BT	414, 512	2.99, 2.42
8.0BT	414, 518	2.99, 2.39

3.3. Photodegradation efficiency of catalyst

Figure 3 presents the photodegradation of the prepared photocatalysts in BPA removal. After adsorption for 66.5 min, the amounts of BPA removed by degradation by T, 0.5BT, 1.0BT, 2.0BT, 4.0BT, 6.0BT and 8.0BT, were 76.4%, 84.9%, 85.5%, 91.5%, 96.2%, 95% and 93.3%, respectively. 4.0BT was the most active photocatalyst. Table 2 presents the kinetic parameters of degradation by the various photocatalysts. The values of the BPA removal rate constant (k) for degradation by T, 0.5BT, 1.0BT, 2.0BT, 4.0BT, 6.0BT, and 8.0BT were 0.0217, 0.0284, 0.0291, 0.0460, 0.0493, 0.0452, 0.0407 min^{-1}, respectively. All of the correlation coefficients exceeded 0.9. The BPA photodegradation rate satisfied pseudo-first-order kinetics. Bi_2O_3/TiO_2 photocatalyst exhibited greater photocatalytic activity than TiO_2.

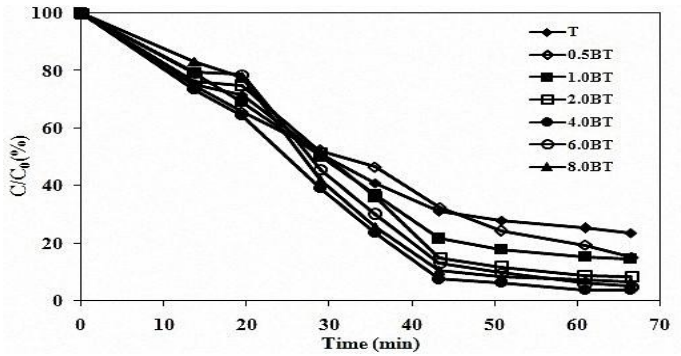

Fig. 3. BPA degradation of various photocatalysts under simulated sunlight (BPA=20 mg/L, pH=6, Q=3.6 cm^3/min, t=66.5 min, λ= 250-1100 nm).

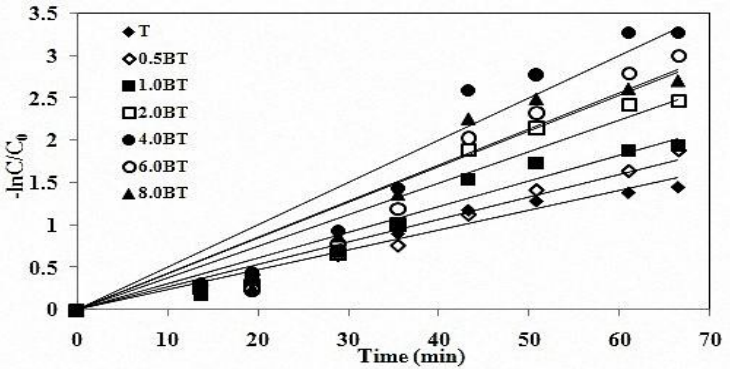

Fig. 4. Simulation of photocatalytic kinetics as pseudo-first-order reaction in various photocatalysts under simulated sunlight.

Table 2
Simulation of kinetic model for aqueous BPA using various photocatalysts under simulated sunlight.

Samples	T	0.5BT	1.0BT	2.0BT	4.0BT	6.0BT	8.0BT
Removal (%)	76.4	84.9	85.5	91.5	96.2	95	93.3
$k\times10^{-2}$ (min^{-1})	2.17	2.84	2.91	4.60	4.93	4.52	4.07
R^2	0.96	0.97	0.95	0.91	0.92	0.92	0.91

Figure 5 shows the durability of the 4.0BT photocatalyst in ten degradations under simulated sunlight. In the first and tenth cycles, the degradation ratios were 94.5% and 91.3%, respectively, revealing a decrease of only 3.2%, suggesting that the Bi_2O_3/TiO_2 photocatalyst exhibited repeatability and photocatalytic activity.

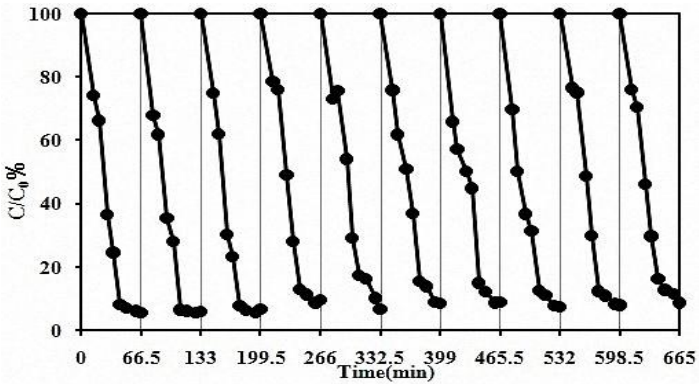

Fig. 5. Durable tests for degradation of aqueous BPA using 4.0BT(BPA=20 mg/L, pH=6, Q=3.6 cm^3/min, t=66.5 min).

4. Conclusion

Bi_2O_3/TiO_2 fixed photocatalysts exhibit obvious photocatalytic activity in the degradation of aqueous BPA under simulated sunlight. After ten uses (665 min) in durability, the 4.0BT photocatalyst removed 88% of BPA. The results of the recycling test revealed the fixed catalytic was effective continuously under simulated sunlight. This study elucidates a feasible industrial route to designing high-performance simulated sunlight.

Acknowledgments and legal responsibility

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