Photodegradation of aqueous bisphenol A using boric acid-doped titanium dioxide
Chao-Yin Kuo, Siang-En Syu and Shiang-Ren Lin

ABSTRACT

A high-photoactivity boric acid-doped titanium dioxide (B-doped TiO2) photocatalyst of the degradation of aqueous bisphenol A (BPA) under sunlight was synthesized and characterized by scanning electron microscope, X-ray photoelectron spectroscopy and UV-vis diffuse reflectance. The band gap energies of TiO2 and B-doped TiO2 (B/Ti mole ratio = 0.2%) were 3.01 and 2.98, showing that B-doped TiO2 could narrow the band gap of pure TiO2. In the photocatalytic kinetics of the photodegradation, the BPA photodegradation rate constants were 1.67 and 1.08 h^-1, respectively. The BPA removal rate satisfies pseudo-first-order kinetics. Results showed that photocatalysts doped with boron displayed greater photodegradation (88% BPA removal) than pure TiO2 (65% BPA removal). Experimental results indicated that B-doped TiO2 not only was an effective photocatalyst, but also had considerable mineralization effects. The recycling test revealed that the photocatalyst remained effective after 10 uses, revealing the stability and reusability.

Key words | bisphenol A, boric acid, photocatalysis, sunlight, titanium dioxide

INTRODUCTION

Bisphenol-A (BPA), which has been listed as an endocrine-disrupting chemical, is widely used. BPA is a monomer that is used in the manufacture of numerous chemical products, such as polycarbonate plastic and epoxy resins (Lee et al. 2004; Tsai et al. 2009). Polycarbonate plastic and epoxy resins are present in many products, such as the linings of food cans, drink packaging, adhesives, baby bottles, fungicide and other products (Tsai et al. 2009; Lu et al. 2013). BPA is reportedly toxic to various organisms (Vanden-berg et al. 2007); it is non-biodegradable and highly resistant to chemical degradation, and its effects on estrogenic and thyroid hormones have been observed in experimental and epidemiological investigations (Gao et al. 2010; Khalil et al. 2014). The health hazard that is represented by BPA and its presence in the environment has already been established. Therefore, a means of environmental BPA removal is required.

Titanium dioxide (TiO2) has various environmental applications due to its high photo-activity, low cost, low toxicity and favorable chemical and thermal stabilities (Rauf & Ashraf 2009; Kuo et al. 2010). However, the large band gap (3.0 eV for rutile and 3.2 eV for anatase) of TiO2 greatly limits its absorption wavelength to less than 387 or 390 nm (Siuzdak et al. 2015; Giannakas et al. 2016), representing only 3–5% of the energy output associated with the spectrum of sunlight, limiting its range of practical applications (Bettinelli et al. 2007; Xing et al. 2009; Kuo et al. 2015; Dozzi & Selli 2016). Therefore, the development of a form of sunlight-sensitive TiO2 is practically important.

In recent years, doping with boron or boric acid to increase the photocatalytic efficiency of TiO2 has been examined (Khan et al. 2008; Lu et al. 2010; Zheng et al. 2011; Zhao et al. 2015). In this work, Degussa P25 and boric acid are used to form B-doped TiO2. The photocatalytic activity of B-doped TiO2 is evaluated by using it in the photodegradation of BPA under artificial visible light and sunlight. The objectives are (a) to measure the absorption wavelength and band gap of the prepared photocatalysts and (b) to compare the
photocatalytic activity of TiO₂ with that of B-doped TiO₂ in the removal of BPA under sunlight.

EXPERIMENTAL METHODS

Chemicals and characterization

BPA (purity > 99%) was purchased from Aldrich. The photocatalyst P25 TiO₂ (purity > 99%, a mixture of anatase and rutile forms of TiO₂ in the ratio 75:25) was obtained from Degussa. Boric acid (purity > 97.5%) was purchased from Alfa Aesar. The pH of the solution was adjusted using nitric acid (HNO₃, 60%) and sodium hydroxide (NaOH, 97%) from Katayama and Kanto, respectively. All chemicals were of analytical reagent grade and used as received.

The elements of photocatalysts were analyzed by X-ray photoelectron spectroscopy (XPS). The morphology and surface topography of the samples were examined by means of scanning electron microscope (SEM) using a JSM-7000F. UV-vis diffuse reflectance spectra were obtained and used to calculate the band gap energy of the photocatalyst. The BPA concentration was measured using a high-performance liquid chromatograph with a UV detector (Agilent Technologies), which was set to a wavelength of 280 nm. Separations were carried out in a Supelcosil C18 column (Supelco). The mobile phase was deionized water and CH₃CN (40:60 v/v); the flow rate was 0.5 mL/min and the injection volume was 20 μL. The total organic carbon (TOC) concentration was measured using an O.I. 1010 TOC analyzer.

Synthesis of boric acid-doped TiO₂

Boric acid at various mole ratios relative to Ti (B/Ti = 0%, 0.06%, 0.08%, 0.2%, 0.4% and 0.6%) was dissolved in 300 mL deionized water. The mixture was squeezed to form a boric acid-doped TiO₂ (length about 2–3 cm and radius about 0.5 cm) as immobilized photocatalyst. The B-TiO₂ photocatalyst was dried at 105 °C and then calcined at 450 °C for 8 h. The obtained B/Ti mole ratios of the prepared immobilized B-TiO₂ were 0.06%, 0.08%, 0.2%, 0.4% and 0.6%; the corresponding compounds are denoted as 0.06BT, 0.08BT, 0.2BT, 0.4BT and 0.6BT, respectively. Degussa P25, without added boric acid, is denoted as T.

Photodegradation experiments

The experiments were performed with the same set-up and conditions as described in the relevant literature (Kuo et al. 2015). The photocatalytic reactor comprised four 30 cm-long quartz tubes. Each tube had an external diameter of 1.2 cm and an internal diameter of 1 cm, and each was filled with 7.9 ± 0.1 g B-doped TiO₂ photocatalyst before 10 mg/L BPA solution was introduced into it using a peristaltic pump. The initial pH of the solution was adjusted to 6. The flow rate of the BPA solution was 1.5 mL/min. The column photo-reactor was irradiated with sunlight.

RESULTS AND DISCUSSION

SEM analysis

Figure 1 presents a detailed SEM image of the surfaces of the formed particles, which reveals that the primary particles are quite uniformly sized and roughly spherical (for samples T, 0.06BT, 0.08BT, 0.2BT, 0.4BT and 0.6BT); samples treated in air at the same temperature show a more uniform grain size and present a similar appearance, because the particle surfaces were composed of TiO₂, which was modified with boric acid to ensure the uniform distribution of grains.

UV-visible analysis

Figure 2 compares the UV-visible spectra of T and BT photocatalysts with various mole ratios (B/Ti = 0.06%, 0.08%, 0.2%, 0.4% and 0.6%) following calcination at 450 °C. Table 1 presents the band gaps of the photocatalysts, calculated using $E_g = 1.239.8/\lambda$, where $E_g$ is the band-gap energy and $\lambda$ is the absorption wavelength.

Figure 2 and Table 1 reveal that the absorption edge of all boric acid-doped TiO₂ was red-shifted toward longer wavelengths. The absorption wavelengths of 0.08BT and 0.2BT were 415 nm, revealing the greatest red shift. The red shift was attributed to the doping with boron, and the
lower band-gap energy of the samples reduced the required driving force to improve the photocatalytic sensitivity. Some researchers reported that the observed red shift is due to the excitation of electrons from the impurity energy levels, located above the valence-band edge (O in 2p), provided by the substituted B atoms, to the conduction band edge (Ti in 3d) (Deng et al. 2014). Similar phenomena were observed in the case of nitrogen and carbon-doped TiO2 (Torres et al. 2004; Neumann et al. 2005). The intensity of modified photocatalysts in the improvement of the photocatalytic sensitivity in the visible region depended on the increases with the amount of boron acid doped (Szkoda et al. 2015).

**XPS spectra**

The oxidation state of the boron dopant was examined by XPS. As shown in Figure 3, the samples contained Ti, O, B and C atoms. The Ti 3p, O 1s, B 1s and C 1s energies were approximately 460, 531, 192.5 and 284.5 eV, respectively. The other detected C atoms were probably present in CO2 spheres that were used during calcination (Li et al. 2015).
In Figure 4, the standard binding energy of B 1s in B2O3 or H3BO3 is around 193.1 eV (B-O bond) (Zaleska 2008; Li et al. 2013; Cavalcante et al. 2015). The standard peak of B 1s consists of two components – one at 192.2 eV, which is assigned to the B-O-B bond, and one at 193.1 eV, which is assigned to the B-O-Ti bond. Figure 5 presents the B-O-Ti and B-O-B structures of the 0.2BT sample, which were evident from the B 1s peak, as a result of the addition of B³⁺ in boric acid, which partially substitutes for Ti⁴⁺, forming B-O-Ti bonds in the crystal lattice of TiO₂. Boron ions were regarded to occur at the interstitial sites of anatase, which can counterpoise the residual charge in TiO₂. In addition, Szkoda et al. (2015) indicated that the location of boron in the interstitial sites was facilitated by the smaller size of Bi³⁺ compared with Ti⁴⁺. The significant amount of boron on the external layer of photocatalysts indicated that the neutrality of the sample could be supported by the surface hydroxyl groups (Feng et al. 2011). This phenomenon improves the efficiency of separation of photo-generated electrons and holes, improving photocatalytic activity (Jaiswal et al. 2016).

### Photocatalytic activity

In this work, the photocatalytic activity of photocatalysts that contained various amounts of boron was tested in the degradation of 10 mg/L BPA. Before irradiation, the BPA was adsorbed in the dark for 66.5 min to reach adsorption equilibrium (Figure 6).

Figure 7 shows the photodegradation of BPA using the prepared photocatalysts. After 66.5 min, T, 0.06BT, 0.08BT, 0.2BT, 0.4BT and 0.6BT had photocatalyzed the removal of 65%, 68%, 86%, 88%, 75% and 66% of the BPA, respectively. All modified samples prepared in this work, in the presence of boron were inactive in the reaction of BPA degradation under sunlight; they revealed stronger absorption in visible region than pure TiO₂. 0.2BT was the most active photocatalyst by photodegradation under sunlight, Doping with boron increased the photocatalytic efficiency of TiO₂ under sunlight because the added B³⁺ in boric acid partially substituted for Ti⁴⁺, forming B-O-Ti bonds in the crystal lattice of TiO₂, enhancing the efficiency of separation of photo-generated electrons and holes and thereby improving photocatalytic activity. These photocatalysts enable the effective use of sunlight.

Generally, the photocatalytic kinetics of the aforementioned degradation is pseudo-first-order. The T, 0.06BT, 0.08BT, 0.2BT, 0.4BT and 0.6BT photocatalysts yielded BPA photodegradation rate constants under sunlight of 1.81, 1.96,
2.38, 2.71, 2.11 and 1.8 h⁻¹, as shown in Table 2. All of the correlation coefficients exceeded 0.9, and the k values of the sunlight systems were consistent with pseudo-first-order kinetics. The rate constant of 0.2BT exceeded that of the T photocatalyst. The results revealed a photocatalytic activity of 0.2BT, which exceeds those of other photocatalysts of this degradation. Most relevant investigations have established that the photodegradation rates of organic compounds can be described using pseudo-first-order kinetics (Wu 2008).

Experiments on durability of photocatalysts

Figure 8 shows the results of 10 degradations using the 0.2BT photocatalyst under sunlight to determine its durability. In the first cycle, the degradation ratio was 88%; after 10 cycles, it still exceeded 82%. Clearly, the BT photocatalyst exhibited favorable repeatability and photocatalytic activity.

Boric acid-doped TiO₂ effect of photocatalytic activity

Recently the possible promotional effect of B as a dopant on the photocatalytic activity of titania has been recognized, and it was found that boron doping could result in absorption of the visible light and B-TiO₂ had higher activity for photo-oxidation of phenol under the visible light irradiation than pure TiO₂ (Fittipaldi et al. 2008; Zaleska et al. 2009; Li et al. 2013; Wang et al. 2014; Cavalcante et al. 2015). Some experimental studies calculated that theoretical densities of states to the O substitution case and revealed that B can be incorporated into the crystal lattice of TiO₂, and the p orbital of B can be mixed with the O₂ orbital, which is responsible for the band gap narrowing, resulting in the broad spectral response of TiO₂ to shift the optical response to the visible range (Chen et al. 2006; Tian et al. 2011; Valentin & Pacchioni 2013). Improving photocatalytic activity of the B-TiO₂ can be interpreted in terms of an increase in either the Ti³⁺ defects or...
oxygen vacancies, the increased surface roughness and the form of impurity states newly introduced by boron doping overlap sufficiently with the 2p electronic states of oxygen. Firstly, since the ion radius of $B^{3+}$ (0.023 nm) is smaller than that of $Ti^{4+}$ (0.064 nm), boron oxides existing at the surface or grain boundary or in the matrix of TiO$_2$ can easily incorporate into the framework of titanium and thus promote an increase in surface defects (oxygen vacancies) (Lu et al. 2010), and could enhance the photocatalytic reaction by acting as an active site to assist the adsorption of the reactant and trap the photo-generated electron to reduce the recombination of $e^-$ and $h^+$. 

### CONCLUSIONS

The photocatalytic activity of prepared boric acid-doped TiO$_2$ photocatalysts under sunlight was evaluated. The 0.2BT photocatalyst removed 88% of BPA in 66.5 min. Clearly, the boric acid-doped TiO$_2$ photocatalyst exhibited photocatalytic activity in the degradation of aqueous BPA under sunlight. Its photocatalytic function was retained after 10 uses, revealing stability and reusability. The results of the recycling test revealed the favorable recyclability of BT photocatalysts under sunlight. The boric acid-doped TiO$_2$ was more active than bare TiO$_2$ for the removal and mineralization of the target compounds due to the effect of boron interstitial positions of TiO$_2$ avoiding the recombination process to some extent.

### ACKNOWLEDGEMENTS

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### REFERENCES


Table 2 | Simulation of kinetic model for aqueous BPA using various photocatalysts under sunlight irradiation

<table>
<thead>
<tr>
<th>Light source</th>
<th>Removal (%)</th>
<th>0.06BT</th>
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<th>0.4BT</th>
<th>0.6BT</th>
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<td>$k \times 10^{-2}$ (min$^{-1}$)</td>
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<td>$R^2$</td>
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<td>0.90</td>
<td>0.96</td>
<td>0.98</td>
<td>0.96</td>
</tr>
</tbody>
</table>

Figure 8 | Durable tests for degradation of aqueous BPA using 0.2BT (BPA $=$ 10 mg/L, pH $=$ 6, Q $=$ 1.5 cm$^3$/min, t $=$ 665 min).


Vandenberg, L. N., Hauser, R., Marcus, M., Olea, N. & Welshons, W. V. 2007 Human exposure to bisphenol A (BPA). Reproductive Toxicology 24, 139–177.


