Synthesis and Characterization of B-S Co-doped TiO₂ Photocatalyst with Variable Boron Concentration

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Abstract. This study aimed to enhance photocatalytic activity of TiO₂ photocatalyst in methylene blue (MB) photodegradation. Boron (B)-sulphur (S) codoped TiO₂ photocatalysts were synthesized using sol-gel method with addition of TTIP as precursor. The reaction was carried out using two dopants (0.05 wt. % of S and 0-7 wt. % of B), stirred for 4 hours followed by washing until pH 7. The samples were dried in oven at 100 °C for 12 hours and calcined at 560 °C with heating rate 5 °C/min. Photodegradation of MB were carried out under ultraviolet (UV) irradiation. The undoped and codoped TiO₂ photocatalysts were characterized using FTIR, XRD and UV-Vis. The presence of TiO₂ peaks (687-719 cm⁻¹) were confirmed using FTIR analysis and thermal analysis of samples has been evaluated using TGA instrument. XRD analysis revealed the presence of anatase phase at 560 °C and the crystallite size (12-22 nm). Undoped and codoped TiO₂ were tested in removing MB from the solution and the results possessed codoped TiO₂ with 3 wt. % of B was the best photocatalyst for this study by degrading 59% and 100% of MB after 10 and 35 minutes, respectively.

1. Introduction
Recently, many manufacturing industries have discarded their unwanted by-products into surroundings and lead to the expansion of environmental pollution problems. There are various of catalytic techniques have been carried out using solar light and artificial light irradiation in order to solve these problems [1]. Despite of other methods, photocatalysis technique has become favourable because of highly promising and efficient method for environmental cleaning. According to Fujishima et al., (2005), it had been three years since the scientific studies on photocatalysis were carried out [2]. Photocatalysis is engaged with the presence of photocatalyst and energy from sunlight.

Photocatalyst such as titanium dioxide (TiO₂), zinc oxide (ZnO), tin (IV) oxide (SnO₂) and cerium (IV) oxide (CeO₂) has been widely used in photocatalytic applications [3, 4, 5, 6]. However the most used photocatalyst is TiO₂ because it possesses an excellent characteristic such as robust, higher photo-activity, eco-friendly, high stability and non-toxicity [7,8]. It also had been extensively used in solar energy conversion and gas sensing field [9]. However, TiO₂ only worked efficiently under UV irradiation and it was able to utilize less than 6 % of solar light because it had band gap energy of 3.2 eV for anatase phase and 3.0 eV for rutile phase, in which the absorption thresholds corresponded to 380 and 410 nm, respectively [10].

The morphology of TiO₂ can be improved by adding double dopants. As mentioned by Livraghi (2009), codoping technique generated synergetic effect which enhanced the properties of final TiO₂ products [11]. An optimum codoping amount can improve the properties of TiO₂ such as larger specific surface area, smaller crystallite size, shifting the absorption edge from UV to visible light region thus preventing the recombination process to occur [12]. Addition of sulphur (S) can improve the photocatalytic efficiency under visible light reaction and boron (B) helps the modification of TiO₂
by inhibiting the crystallite size, increasing the surface area as well as inducing the crystalline process [13, 14]. In this study, sol gel method was used because it is reproducible and can lead to nanoparticles, meso to macroporous materials, high purity and high surface area [15]. Samples were characterized using Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), X-ray diffraction (XRD) and ultraviolet-visible spectroscopy (UV-Vis).

1.1 Photocatalytic Mechanism of TiO₂

Generation of electron-hole pairs in photocatalytic reaction

\[ \text{TiO}_2 + h_v \rightarrow e_{cb}^- + h_{vb}^+ \]

(1)

Formation of superoxide radical anion (O₂ •⁻)

\[ e_{cb}^- + O_2 \rightarrow O_2 •^- \]

(2)

Formation of hydroxyl radical (H⁺) and surface adsorbed hydroxyl radical (• OH<sub>ad</sub>)

\[ h_{vb}^+ + H_2O \rightarrow • OH + H^+ \]

(3)

\[ h_{vb}^+ + OH^- \rightarrow • OH_{ad} \]

(4)

Recombination of electron and positive hole due to the abundance of electron occurs in conduction band

\[ e_{cb}^- + h_{vb}^+ \rightarrow \text{TiO}_2 \]

(5)

Complete photocatalytic oxidation process has oxidize organic pollutant into salts, carbon dioxide (CO₂) and water (H₂O)

\[ • OH + \text{pollutant} + O_2 \rightarrow \text{Products} \text{ (salts, CO}_2, \text{H}_2\text{O)} \]

(6)

2. Methodology

Boron oxide (B₂O₃) and thiourea (CH₄N₂S) were used as the source of B and S respectively. 200 mL of cold distilled water was added into a beaker. While stirring, 18.5 mL of titanium (IV) isopropoxide (TTIP) was added into the beaker and stirred for 30 minutes. Under continuous stirring, 1 wt. % of B₂O₃ and 0.05 wt. % of CH₄N₂S were successively added into the solution, followed by adding glacial acetic acid (CH₃COOH). Stirring was continued for 3 hours. Then, 50 mL of 10 M sodium hydroxide (NaOH) was poured into the mixture and stirred for 30 minutes. Mixture was washed using distilled water until pH 7. The precipitate was dried in oven at 100 °C for 12 hours. Dried powder was crushed into finer powder and calcined at 560 °C. All steps were repeated for 0, 3, 5, 7 wt.% B. Samples were labelled as pure TiO₂, TiO₂:S0.05.B1, TiO₂:S0.05.B3, TiO₂:S0.05.B5 and TiO₂:S0.05.B7. All samples were characterized using FTIR, TGA, XRD and UV-Vis.

3. Results and Discussion

3.1 FTIR

In this study, IR spectra was analysed using potassium bromide (KBr) pellet technique and the IR spectrum of synthesized pure and co-doped TiO₂ photocatalysts were in the range of 4000-450 cm⁻¹ wavenumber.
Figure 1. FTIR spectra of pure and co-doped TiO$_2$

The obtained FTIR spectra in Figure 1 showed the following main patterns. The strong absorption band at 3367-3396 cm$^{-1}$ and 1624-1635 cm$^{-1}$ are attributed to O-H stretching and bending vibration which comes from water absorbed on the TiO$_2$ surfaces and hydrogen-bonded hydroxyl groups [16,17]. It is in agreement with the statement from Mahalingam (2017), which stated that the broad band which corresponds to –OH stretching was recorded in the range of 3000–3500 cm$^{-1}$ [18]. The absorption range around 1630 cm$^{-1}$ may be related to hydroxyl (bending) groups of molecular water [19]. Peaks appeared at 1220 belonged to the B–O bond in the B$_2$O$_3$ crystal as reported by Chen (2006) [17]. Functional group of S was not identified due to its small amount used in this study. The strong absorption observed at 687-719 cm$^{-1}$ is attributed to lattice vibrations of TiO$_2$. Lu et al. (2008) mentioned that the broad absorption band appeared at 500-1000 cm$^{-1}$ was ascribed to the stretching vibration absorption of the Ti-O-Ti linkages in TiO$_2$ nanoparticles. The calcination of TiO$_2$ powders at 560 °C lead to significant sharpening of absorption bands in the region of 400-700 cm$^{-1}$ and clearly indicates the formation of anatase phase [20]. There is no peak appeared at 2900 cm$^{-1}$ in all spectrum which indicates that all organic compounds (C-H stretching band) decomposed from the samples after calcination [21]. The results revealed that addition of dopants will narrow the band gap of TiO$_2$ leading to improvement in the performance of photocatalytic activity.

3.2 Thermo-gravimetric Analysis

Thermal properties of synthesized pure and co-doped TiO$_2$ are shown in Figure 2. All samples were examined from room temperature to 900 °C with heating rate 10 °C/min. The trend showed decreasing in weight loss and followed with plateau as the temperature increased to 900 °C. The weight loss of samples decreased with the addition of dopant. Among all curves, pure TiO$_2$ showed a larger overall weight loss. The significant weight lost was approximately 10.40 to 16.23% which occurred before 250 °C. As the temperature increased up to 400 °C, the decomposition of 3 to 4 % organic compounds (non-reactive titanium precursor) occurs along with the elimination of OH groups attached on the surface of synthesized TiO$_2$ nanoparticles [22, 23, 24]. Doped samples results confirmed a denser microstructure and lower surfaces area has caused less water absorption compared to undoped TiO$_2$ [25]. After 400 °C, the thermo-gravimetric curves showed plateau characteristic.
3.3 X-ray Diffraction

XRD analysis was carried out to determine the crystalline phase and to estimate the crystallite size of synthesized TiO$_2$ photocatalyst. Figure 3 displays the XRD diffractograms of pure and codoped TiO$_2$ photocatalyst calcined at 560 °C.

All samples were confirmed the presence of anatase phase of titania with the corresponding (101) plane of high intensity for both pure and codoped TiO$_2$ (JCPDS No. 21-1272). The peaks centered at 25.37, 37.99, 48.12, 54.26, 57.23, 62.79, 68.85, 70.44 and 75.15 ° are corresponding to anatase (101), (004), (200), (105), (211), (204), (116), (220) and (301) crystal planes, respectively. It can be observed that the increasing in B weight does not alter the polymorph of TiO$_2$. The peak of B and S was not detected, and this may due to good incorporation and dispersion of dopant into TiO$_2$ lattice.
The results revealed the presence of crystalline phase along with pure anatase phase when the samples were calcined at 560 °C. The crystalline sizes were calculated using Sherrer’s equation in Equation 1 [20]:

\[ D = \frac{k\lambda}{\beta \cos \theta} \]  

Where D is the crystallite size in nanometer (nm), k is a constant (0.9), with the assumption of spherical particles), \( \lambda \) is the wavelength of the X-ray radiation (CuK\( \alpha \) = 0.1541 nm), \( \beta \) is the full width at half maximum (FWHM) of selected peak and \( \theta \) is the diffraction angle for the peak (Bragg’s angle).

Table 1 shows the crystallite sizes decreased as the amount of boron increased to 3 wt.% and increased as the amount of boron exceeded 3 wt.%. This is because the addition of dopants will suppress the crystallite size of photocatalyst due to the insertion of dopant into the lattice structure of TiO\(_2\) octahedral thus altering its properties [12].

| Photocatalyst       | Crystallite size (nm) | Peak assignment |
|---------------------|-----------------------|-----------------|
| Undoped TiO\(_2\)  | 22                    | Anatase TiO\(_2\) |
| TiO\(_2\).S0.05.B1  | 12                    | Anatase TiO\(_2\) |
| TiO\(_2\).S0.05.B3  | 12                    | Anatase TiO\(_2\) |
| TiO\(_2\).S0.05.B5  | 15                    | Anatase TiO\(_2\) |
| TiO\(_2\).S0.05.B7  | 15                    | Anatase TiO\(_2\) |

### 3.4 Photogedradation of MB

The findings showed that the degradation rate was directly proportional to increasing of time. As depicted in Figure 4, the graph showed a similar trend. However, by comparing codoped TiO\(_2\) and pure TiO\(_2\), the findings portrayed that codoped TiO\(_2\) showed a better performance compared to pure TiO\(_2\) [26, 27]. Addition of dopant into TiO\(_2\) may alter the properties of photocatalyst by narrowing the band gap, lessening crystallite size and increasing the surface area, leading to higher absorption of dye molecules [28].

All samples were successfully degrading MB at different irradiation time. It reached a maximum activity at 3 and 5 wt.% of boron dopant and the performance decreased with increasing B concentration. The performance of 7 wt.% B doping was slower compared to 3 wt.% B doping but faster than pure TiO\(_2\). Addition of 3 wt.% of B improved the performance of photocatalyst by degrading 100% MB at 35 min of UV irradiation as compared to 65 minutes of pure photocatalyst. However, as the doping concentration increased to 7 wt.%, it showed a decrease in degradation rate and it was fully absorbed dye molecules at 45 min of UV irradiation.

These results indicated that the performance of TiO\(_2\) photocatalyst can be improved by adding appropriate amount of dopant and its performance can be deteriorated when excessive amount of dopant was added into TiO\(_2\) photocatalyst [12]. The deterioration may due to the recombination by reducing the opportunity of oxygen photo-adsorbed on the surface of TiO\(_2\) to react with free electrons to form O\(^2-\) ion or the corresponding hole to form \( \cdot \)OH radical [12]. Formation of diboron trioxide phase after exceeding the optimal doping also inhibits the photocatalytic activity of photocatalyst [29]. Addition of S and B as codoping agent helps to promote the photocatalytic performance by suppressing the growth of TiO\(_2\) nanoparticles as well as increasing the surface area thus enhancing the
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photo
catalytic performance [13, 14, 30]. Hence, the photocatalytic activity was optimal when the
doping amount of boron was 3 wt. %.

Figure 4. Effect of different composition of boron towards degradation rate of MB

4. Conclusion
Pure and codoped TiO2 photocatalysts were synthesized via sol gel method and TTIP as a precursor. Formation of TiO2 and the presence of boron were confirmed by FTIR. TGA results also demonstrated that there was significant mass loss in pure TiO2. All samples showed a pure anatase peak with crystalline size ranging from 12 to 22 nm and incorporation of dopants were examined using XRD analysis. The codoped TiO2 exhibited a higher photodegradation rate for MB under UV irradiation compared to pure TiO2. Exceeding optimum amount of dopant deteriorated the photocatalytic performance. 3 wt. % was identified as the optimal composition for the best photodegradation in this research.

5. References
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