



# Article Visible Light Responsive Strontium Carbonate Catalyst Derived from Solvothermal Synthesis

Pornnaphat Wichannananon<sup>1,2</sup>, Thawanrat Kobkeatthawin<sup>2</sup> and Siwaporn Meejoo Smith<sup>2,\*</sup>

- <sup>1</sup> Center of Excellence for Innovation in Chemistry, Faculty of Science, Mahidol University, 272 Rama VI Rd., Rajthevi, Bangkok 10400, Thailand; pornnaphat.w@gmail.com
- <sup>2</sup> Center of Sustainable Energy and Green Materials and Department of Chemistry, Faculty of Science, Mahidol University, 999 Phuttamonthon Sai 4 Road, Salaya, Nakorn Pathom 73170, Thailand; kunthidakob@gmail.com
- \* Correspondence: siwaporn.smi@mahidol.edu; Tel.: +66-93593-9449

Received: 24 July 2020; Accepted: 11 September 2020; Published: 17 September 2020



Abstract: A single crystalline phase of strontium carbonate (SrCO<sub>3</sub>) was successfully obtained from solvothermal treatments of hydrated strontium hydroxide in ethanol (EtOH) at 100 °C for 2 h, using specific Sr:EtOH mole ratios of 1:18 or 1:23. Other solvothermal treatment times (0.5, 1.0 and 3 h), temperatures (80 and 150 °C) and different Sr:EtOH mole ratios (1:13 and 1:27) led to formation of mixed phases of Sr-containing products, SrCO<sub>3</sub> and Sr(OH)<sub>2</sub> xH<sub>2</sub>O. The obtained products (denoted as 1:18 SrCO<sub>3</sub> and 1:23 SrCO<sub>3</sub>), containing a single phase of SrCO<sub>3</sub>, were further characterized in comparison with commercial SrCO<sub>3</sub>, and each SrCO<sub>3</sub> material was employed as a photocatalyst for the degradation of methylene blue (MB) in water under visible light irradiation. Only the 1:23 SrCO<sub>3</sub> sample is visible light responsive ( $E_g = 2.62 \text{ eV}$ ), possibly due to the presence of ethanol in the structure, as detected by thermogravimetric analysis. On the other hand, the band gap of 1:18 SrCO<sub>3</sub> and commercial SrCO<sub>3</sub> are 4.63 and 3.25 eV, respectively, and both samples are UV responsive. The highest decolourisation efficiency of MB solutions was achieved using the 1:23 SrCO<sub>3</sub> catalyst, likely due to its narrow bandgap. The variation in colour removal results in the dark and under visible light irradiation, with radical scavenging tests, suggests that the high decolourisation efficiency was mainly due to a generated hydroxyl-radical-related reaction pathway. Possible degradation products from MB oxidation under visible light illumination in the presence of SrCO<sub>3</sub> are aromatic sulfonic acids, dimethylamine and phenol, as implied by MS direct injection measurements. Key findings from this work could give more insight into alternative synthesis routes to tailor the bandgap of SrCO<sub>3</sub> materials and possible further development of cocatalysts and composites for environmental applications.

Keywords: strontium carbonate (SrCO<sub>3</sub>); solvothermal method; photocatalysis; visible light

# 1. Introduction

Textile industries employ over 10,000 dyes and pigments in the manufacturing of cotton, leather, clothes, wool, silk and nylon products [1–3]. An estimated 700,000 tons or more of synthetic dyes are thought to be annually discharged into the environment [4], causing serious water pollution as many of these dyes are toxic, highly water soluble and highly stable against degradation by sunlight or increased temperature [5]. Therefore, effective treatments of dye-contaminated water have continuingly received great attention by academic and industrial sectors. Various wastewater treatment methods have been applied to remove toxic dyes from wastewater, such as coagulation–flocculation, adsorption, membrane separation, biodegradation and oxidation processes [6]. Among these methods, photocatalytic oxidation processes have been proven to be simple and effective at organic dye decomposition, forming relatively

low toxic by-products with potential mineralization to generate  $CO_2$  and  $H_2O$  [7–9]. In this process, under light irradiation a semiconducting catalyst absorbs photon energy promoting electron transfer from the valence band (VB) to the conduction band (CB), resulting in electron-hole pair generation. The generated holes (h+) further react with water molecules while the electrons (CB) react with oxygen, resulting in formation of active hydroxyl (•OH) and superoxide (•O<sub>2</sub><sup>-</sup>) radicals, respectively. The •OH radicals subsequently attack organic pollutants in water leading to oxidative degradation of pollutants.

Wide bandgap TiO<sub>2</sub> [10] and ZnO [11] semiconducting materials have proven to be efficient catalysts for the photo-oxidation of organic pollutants in water. However, these require high-energy ultraviolet irradiation, which requires special and costly safety protocols to be in place for the use of these materials in wastewater treatment. An attractive alternative is to use harmless visible light sources in the photoreactor, employing a visible light responsive photocatalyst for pollutant degradation. Such visible light responsive photocatalysts need to promote the photo-oxidative degradation of pollutants using sunlight (7% UV and 44% visible light emission, and other low-energy radiations [12]) to ensure wastewater treatment is a sustainable process. Strontium carbonate ( $SrCO_3$ ) is a common starting material for the manufacture of colourants in fireworks, glass cathode-ray tubes and computer monitors [13,14]. While commercially available SrCO<sub>3</sub> material is commonly derived from celestine (SrSO<sub>4</sub>) mineral via calcination followed by Na<sub>2</sub>CO<sub>3</sub> treatment (the black ash method) [15], synthetic  $SrCO_3$  can be obtained using calcination and wet chemical methods under ambient [16,17] or high-pressure [18] atmospheres. Table 1 summarizes the key features (synthesis conditions, characteristics and the bandgap energy) of synthetic  $SrCO_3$  in the literature. Methylene blue, a cationic organic dye and a common colouring agent used in cotton, wood, silk [19] cosmetics, and textile [20] dying is a frequently utilized representative dye pollutant mimicking those present in industrial effluents. Song and coworkers reported effective methylene blue (MB) degradation under visible light irradiation ( $\lambda > 400$  nm) after 3 h treatment with SrCO<sub>3</sub> obtained from the calcination of synthetic  $Sr(OH)_2$  [21], while Molduvan and coworkers reported the removal of MB from aqueous solutions using a commercial natural activated plant-based carbon [22]. Other works have utilized SrCO<sub>3</sub> as a cocatalyst incorporated in photocatalyst composites, e.g., Ag<sub>2</sub>CO<sub>3</sub>/SrCO<sub>3</sub> [23],  $TiO_2/SrCO_3$  [24] and  $SrTiO_3/SrCO_3$  [25], to expand the photoresponsive range of the material and to improve its catalytic activity and reaction selectivity.

Conditions	Reaction Time	Morphology	Band Gap	References
Celetine ore (SrSO <sub>4</sub> ) (industrial scale)	Reductive calcination followed by Na <sub>2</sub> CO <sub>3</sub> (aq) assisted precipitation (the black ash method)	-	-	[26]
Celetine ore (SrSO <sub>4</sub> ) (industrial scale)	Double decomposition in Na <sub>2</sub> CO <sub>3</sub> (aq)	-	-	[27]
$Sr(OH)_2 + CO_2 + EDTA$	50 °C, 10 min	spherical shape	-	[28]
$Sr(NO_3)_2 + TEA + NaOH$	100 °C, 12 h	branchlet-like SrCO3 nanorods	-	[17]
$SrCl_2 + H_2O + DMF + glycerol$	120 °C, 8 h	flower shape	-	[29]
$Sr(NO_3)_2 + urea$	120 °C, 24 h	urchin-like SrCO <sub>3</sub>	-	[30]
Sr(NO <sub>3</sub> ) <sub>2</sub> + (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> + HMT	Room temp, 7 days	branch-like, flower-like, capsicum-like	-	[31]
CH <sub>3</sub> COO <sub>2</sub> Sr + Na <sub>2</sub> SO <sub>4</sub> + hexamethylene triamine	160 °C, 24 h	spherical shape	3.17	[32]
$Sr(NO_3)_2 + Na_2CO_3$	120 °C, 8 h	various shapes such as rod shape ellipsoid shape sphere shape	-	[33]
1. $SrCl_2 + Na_2CO_3$ 2. $SrCl_2 + CO(NH_2)_2$ 3. $SrCl_2 + CO(NH_2)_2 + SDS$	1. 110 °C, 12 h 2. 110 °C, 12 h 3. 110 °C, 12 h	rod shape rod shape flower shape	-	[34]
$Sr(OH)_2$ + flowing CO <sub>2</sub> gas	1. 50 °C, 12 h 2. 60 °C, 12 h 3. 70 °C, 12 h	nanowhisker rod shape pherical shape	-	[35]

Table 1. Synthesis, key characteristics and bandgap energy of synthetic SrCO<sub>3</sub>.

This work investigated the effects of precursor concentrations (Sr:ethanol mole ratios), solvothermal temperatures and treatment times on the properties of  $SrCO_3$  materials and their photocatalytic degradation of MB in water under visible light irradiation, as a function of pH and temperature. Kinetic and mechanistic studies of the MB degradation process were carried out through reaction rate determination and identification of the end-products. The photocatalytic performance of synthesized  $SrCO_3$  was compared with that of commercially available material, in order to derive insights into the relationships between properties and catalytic activity.

## 2. Results and Discussions

## 2.1. Effects of Synthesis Conditions

Solvothermal treatments of strontium nitrate in ethanol (EtOH) were carried out at various temperatures (80, 100 and 150 °C), treatment times (0.5, 1, 2 and 3 h) and Sr:EtOH mole ratios (1:13, 1:18, 1:23 and 1:27). From powder X-ray diffraction (PXRD) results in Figure 1, a single phase of SrCO<sub>3</sub> was obtained from two conditions: 2 h solvothermal treatment at 100 °C using a Sr:EtOH mole ratio of 1:18 or 1:23. These samples are denoted as 1:18 SrCO<sub>3</sub> and 1:23 SrCO<sub>3</sub> in further discussions. Notably, mixed phases of SrCO<sub>3</sub> and hydrated strontium hydroxides (Sr(OH)<sub>2</sub>·xH<sub>2</sub>O, where x is the number of molar coefficient of water in strontium hydroxide solid) were obtained from all other synthesis conditions (results shown in Supplementary Materials: Figures S1 and S2). Typical diffraction peaks correspond well with (110), (111), (021), (002), (012), (130), (220), (221), (132) and (113) orthorhombic SrCO<sub>3</sub> lattice planes [34,36], whereas other diffraction peaks match with those of previously reported Sr(OH)<sub>2</sub>·H<sub>2</sub>O [37] and Sr(OH)<sub>2</sub>·8H<sub>2</sub>O phases [38]. The formation of Sr(OH)<sub>2</sub> xH<sub>2</sub>O is possibly due to adsorbed alcohol, promoting the addition of OH functional groups on the solid surface [39], upon solvothermal crystallization of Sr-containing products.



**Figure 1.** PXRD patterns of Sr-containing samples derived from 2 h solvothermal treatments of hydrated strontium hydroxide in ethanol at various Sr:EtOH mole ratios (1:13, 1:18, 1:23 or 1:27) at 100 °C.

FTIR spectra of the prepared Sr-containing samples are shown in Figure 2. The absorption bands located within 1700–400 cm<sup>-1</sup> regions were attributed to the vibrations in  $CO_3^{2-}$  groups. The strong broad absorption at 1470 cm<sup>-1</sup> was considered to be due to an asymmetric stretching vibration, and the sharp absorption bands at 800 cm<sup>-1</sup> and 705 cm<sup>-1</sup> can be specified to the bending out-of-plane vibration and in-plane vibration, respectively. The weak peak at 1770 cm<sup>-1</sup> indicated a combination of vibration modes of the  $CO_3^{2-}$  groups and  $Sr^{2+}$ . The sharp peak at 3500 cm<sup>-1</sup> was assigned to the stretching mode of –OH- in  $Sr(OH)_2$ , and the broad absorption peak around 2800 cm<sup>-1</sup> was assigned to the stretching mode of H<sub>2</sub>O in  $Sr(OH)_2$ ·H<sub>2</sub>O and  $Sr(OH)_2$ ·8H<sub>2</sub>O. These results are consistent with the commercial  $SrCO_3$  and the 1:18  $SrCO_3$  and 1:23  $SrCO_3$  samples being of similar chemical composition.



**Figure 2.** FTIR spectra of Sr-containing samples derived from 2 h solvothermal treatment of hydrated strontium hydroxide in ethanol at various Sr:EtOH mole ratios (1:13, 1:18, 1:23 or 1:27) at 100 °C.

SEM images of the obtained SrCO<sub>3</sub> materials (derived from Sr:EtOH mole ratios of 1:18 or 1:23) are compared with those of commercial SrCO<sub>3</sub> in Figure 3. Whisker-like SrCO<sub>3</sub> and spherical particles were obtained under these respective synthesis conditions. Figure 3c highlights the relatively large rod-like particles of commercial SrCO<sub>3</sub>. Variation in particle sizes was observed in solvothermally obtained SrCO<sub>3</sub>, with particle sizes being smaller for the 1:18 SrCO<sub>3</sub> samples. Notably, commercial SrCO<sub>3</sub> contains much larger particles than those of the synthesized material. From literature [26,27], SrCO<sub>3</sub> production plants utilize two common methods, the black ash method and the soda method, in conversion of celestine ore (SrSO<sub>4</sub>) to SrCO<sub>3</sub> (Table 1). The black ash method involves high-temperature calcination of the ore to obtain SrS, with crystalline SrCO<sub>3</sub> solid being formed after dissolving the SrS in aqueous Na<sub>2</sub>CO<sub>3</sub>, followed by precipitation. The soda method produces SrCO<sub>3</sub> through the two-step decomposition reaction between celestine and aqueous Na<sub>2</sub>CO<sub>3</sub>, to obtain precipitated SrCO<sub>3</sub>. From this information, as the formation of commercial SrCO<sub>3</sub> does not require high temperatures (>150 °C) for solvent evaporation and precipitation of SrCO<sub>3</sub>, the larger grain size of the commercial SrCO<sub>3</sub> sample is probably due to the fast solvent evaporation during the precipitation processes.



**Figure 3.** SEM images of SrCO<sub>3</sub> derived from 2 h solvothermal treatment at 100 °C, using Sr:EtOH mole ratios of (**a**) 1:18 and (**b**) 1:23 compared with (**c**) commercial SrCO<sub>3</sub>.

Thermogravimetric analysis (TGA) plots (Figure 4) suggest thermal stability of all SrCO<sub>3</sub> samples up to 600 °C. Slight weight loss (<1%) was likely due to moisture or solvent residue [40]. The 1:23 SrCO<sub>3</sub> sample gives a relatively high weight loss of 0.21%, which corresponds to the removal of surface adsorbed moisture and ethanol (weight loss upon heating up to 400 °C) and the loss of ethanol from the SrCO<sub>3</sub> lattice at ca. 450 °C. Decomposition of SrCO<sub>3</sub> takes place at temperatures above 800 °C as a result of conversion to SrO.



**Figure 4.** Thermogravimetric analysis (TGA) plots of SrCO<sub>3</sub> samples prepared using Sr:EtOH mole ratios of 1:18 and 1:23, compared with that of commercial SrCO<sub>3</sub>.

Based on the PXRD and TGA results, chemical transformation of hydrated strontium hydroxide in the presence of ethanol under solvothermal treatments leads to the formation of  $SrCO_3$  and ethanol incorporated  $SrCO_3$  materials, as proposed by the reactions below. In general,  $CO_2$  in air can react with strontium hydroxide to form  $SrCO_3$ , which precipitates after the sonication step and solvothermal treatments. Ethoxide could be formed under basic conditions, resulting in an  $CH_3CH_2O\cdots Sr^{2+}\cdots OCH_2CH_3$  intermediate, which is subsequently transformed to ethanol incorporated in  $SrCO_3$ . Note that the amount of ethanol incorporated within the  $SrCO_3$  is sufficiently low, such that a single phase of  $SrCO_3$  was observed in PXRD pattern of the 1:23  $SrCO_3$  sample.

$$Sr(OH)_2 + CO_2 \rightarrow SrCO_3 + H_2O$$
  
 $Sr(OH)_2 + CO_2 \rightleftharpoons Sr^{2+} + HCO_3^- + OH^-$ 

$$HCO_{3}^{-} + OH^{-} \rightarrow CO_{3}^{2-} + H_{2}O$$

$$CH_{3}CH_{2}OH + OH^{-} \rightleftharpoons CH_{3}CH_{2}O^{-} + H_{2}O$$

$$Sr(OH)_{2} + H_{2}O \rightleftharpoons Sr^{2+} (aq) + OH^{-} (aq)$$

$$Sr^{2+} + 2CH_{3}CH_{2}O^{-} \rightarrow Sr^{2+} ... 2OCH_{2}CH_{3}$$

$$Sr^{2+} ... OCH_{2}CH_{3} + HCO_{3}^{-} \rightarrow SrCO_{3} ... HOCH_{2}CH_{3}$$

#### 2.2. Optical Properties

UV–VIS diffuse reflectance spectra of the 1:18 SrCO<sub>3</sub>, 1:23 SrCO<sub>3</sub> and commercial SrCO<sub>3</sub> in Figure 5a showed that the characteristic absorption edge of the 1:23 SrCO<sub>3</sub> sample is located in the visible light region (473 nm), whereas the spectral response of other SrCO<sub>3</sub> samples was observed in the UV region, with absorption band edges of 268 and 381 nm for the 1:18 SrCO<sub>3</sub> sample and commercial SrCO<sub>3</sub>, respectively. The band gap energy values suggested by Kubelka–Munk plots (Figure 5b) are 4.63 and 3.25 eV for 1:18 SrCO<sub>3</sub> and commercial SrCO<sub>3</sub>, respectively. By contrast, the bandgap energy of the 1:23 SrCO<sub>3</sub> sample is 2.62 eV, and its visible response is possibly due to the presence of incorporated ethanol in the solid sample, as suggested by TGA results.



**Figure 5.** (a) UV-visible diffuse reflectance spectra and (b) Kubelka–Munk plots of the SrCO<sub>3</sub> synthesized at Sr:EtOH mole ratios of 1:18 and 1:23, compared with those of commercial SrCO<sub>3</sub>.

#### 2.3. Decolourisation of Methylene Blue (MB)

Figure 6a illustrates the colour removal efficiencies of 10 ppm MB aqueous solutions in the dark and under visible light irradiation after 1 h treatment with SrCO<sub>3</sub>. Similar colour removal efficiencies from treatment of MB(aq) with 1:18 SrCO<sub>3</sub> in the dark and under light illumination suggested major adsorption processes occurred due to the wide bandgap of the 1:18 SrCO<sub>3</sub> sample. On the other hand, the visible responsive 1:23 SrCO<sub>3</sub> and commercial SrCO<sub>3</sub> gave higher colour removal efficiencies under irradiation conditions than those from dark experiments, implying both adsorption and photodegradation of MB are of importance. Therefore, from these catalyst screening tests, the colour removal efficiencies of aqueous MB solutions strongly depend on the bandgap energy of SrCO<sub>3</sub> materials and that the 1:23 SrCO<sub>3</sub> is the most active catalyst. Figure 6b demonstrates that only low colour removal efficiencies occur due to adsorption (in the dark) and photolysis (irradiation and no SrCO<sub>3</sub>). Treatments of dye solutions with 1:23 SrCO<sub>3</sub> is much less effective (low colour removal efficiency) under dark conditions in comparison to decolourisation under visible light irradiation. These results suggest that the main process of MB colour removal is caused by photocatalytic treatment by using the SrCO<sub>3</sub> photocatalyst rather than adsorption.



**Figure 6.** (a) Colour removal efficiencies of 10 ppm methylene blue (MB) aqueous solution in the dark, and under visible light irradiation in the presence of SrCO<sub>3</sub>. (b) Absorption spectra of MB in the dark or under visible light irradiation by SrCO<sub>3</sub> (1:23 and 1:18). All decolourisation experiments were performed at 30 °C using SrCO<sub>3</sub> with catalyst loadings of 4.0 g·L<sup>-1</sup> with 1 h treatment.

The percentage of MB colour removal after treatment with  $SrCO_3$  photocatalyst (sample 1:23) is shown in Figure 7a. When a suspension of  $SrCO_3$  in 10 ppm fresh MB solution was kept in the dark for 3 h, the concentration of dye slightly decreased, while the colour of the dye solution remained unchanged. It was observed that the absorption capacity of MB on the  $SrCO_3$  surface is negligible because the specific area of the prepared  $SrCO_3$  photocatalyst is low (9.23 m<sup>2</sup>·g<sup>-1</sup>). Upon visible irradiation, the prepared  $SrCO_3$  gave a high percentage of MB colour removal (>99% after 3 h visible irradiation).



**Figure 7.** (a) Colour removal efficiencies of 10 ppm MB aqueous solution (pH 5.5) as a function of time in the dark or under visible light irradiation; adsorption of MB into SrCO<sub>3</sub> (loading 4 g·L<sup>-1</sup>) in the dark, MB photolysis and photocatalysis of MB under visible light illumination catalyzed by SrCO<sub>3</sub> (loading 4 g·L<sup>-1</sup>). (b) Effects of a scavenger (tert-BuOH) on the colour removal efficiency of 10 ppm MB after 3 h treatment with the 1:23 SrCO<sub>3</sub> (4 g·L<sup>-1</sup>).

In order to prove that hydroxyl radicals (•OH) are the active species in the photocatalytic degradation process, experiments were conducted in the presence of a radical scavenging reagent. One such reagent, tert-butyl alcohol (tert-BuOH), if present, should significantly inhibit the oxidation of MB [41]. The result in Figure 7b indicates that after treatment for 3 h, adding tert-BuOH resulted in poor colour removal efficiencies (6.90%), whereas in the absence of the reagent very high colour removal efficiencies (>99%) were achieved. The formation of a product arising from the reaction

between tert-BuOH and •OH as ascribed through a radical pathway [41] thus resulted in the poor activity, confirming that hydroxyl radicals are the important active species assisting MB degradation.

The effect of pH on the MB decolourisation under visible light irradiation was examined over a range of pH 3–9. The colour removal efficiency reached 73% after 1 h treatment at pH 3, while lower colour removal efficiencies were obtained at pH 5.5 (51%), pH 7 (42%) and pH 9 (29%) over the same time period, as shown in Figure 8a. In addition, the natural logarithm of the MB concentrations was plotted as a function of irradiation time, affording a linear relationship, as presented in Figure 8b. Using the first-order model, the highest rate constant of MB colour removal was obtained at pH 3, with the degradation being slowest at pH 9. The decreasing rate constants of MB decolourisation with increasing pH may be the result of the presence of carbonate ( $CO_3^{2-}$ ) and hydroxide (OH<sup>-</sup>) ions, which are radical scavengers [42,43]. At pH 5.5–10, the low colour removal efficiencies may be due to the following reactions.

$$CO_3^{2-} + \bullet OH \rightarrow CO_3^{\bullet-} + OH^-$$
  
 $OH^- + \bullet OH \rightarrow H_2O + O^-$ 



**Figure 8.** (a) Colour removal efficiencies of 10 ppm MB aqueous solution with time, using  $SrCO_3$  as photocatalyst. (b) Kinetics of MB decolourisation catalyzed by  $SrCO_3$  as a function of pH. All decolourisation experiments were performed using  $SrCO_3$  with catalyst loading of 4.0 g·L<sup>-1</sup> at 30 °C from pH 3–9.

The effect of temperature on the degradation of MB as a function of time is discussed in Figure 9. From Figure 9a, it can be observed that higher temperatures result in higher MB colour removal efficiencies. Under visible light irradiation, the MB colour removal efficiency reached 100% after 1 h treatment at 70 °C. In all cases MB concentrations decrease with irradiation time. The linear plots between the natural logarithm of the MB concentration versus irradiation time are shown in Figure 9b, which indicate that the decolourisation process follows first-order kinetics. The rate constants of MB decolourisation increased with temperature, indicating that MB removal by 1:23 SrCO<sub>3</sub> is overall endothermic. The 1:23 SrCO<sub>3</sub> sample is rather stable during the photocatalytic MB degradation reaction, as only negligible concentrations of Sr (<10 ppm) were detected in the treated MB solution.



**Figure 9.** (a) Colour removal efficiencies of 10 ppm MB aqueous solution (pH 5.5) over time using SrCO<sub>3</sub> as photocatalyst. (b) Kinetics of MB decolourisation catalyzed by SrCO<sub>3</sub> as a function of temperature. All decolourisation experiments were performed using 1:23 SrCO<sub>3</sub> with catalyst loading of 4.0 g·L<sup>-1</sup> at temperatures 20–70 °C.

## 2.4. Degradation Products

Figure 10 highlights mass spectra generated from the MB degradation products with the mass-to-charge ratios (m/z) of 77, 122, 234, 284 and 303, reported with the possible fragmented ions shown accordingly.



**Figure 10.** Mass spectra of intermediates from the MB degradation after treatment for (**a**) 10 min, (**b**) 25 min and (**c**) 60 min. All experiments were performed by suspending 1:23 SrCO<sub>3</sub> in 10 ppm MB ( $4 \text{ g} \cdot \text{L}^{-1}$  of MB solution) followed by visible light illumination.

The proposed reaction pathway of MB photooxidation over SrCO<sub>3</sub> photocatalyst is outlined in Figure 11. The detected degradation products, as identified from fragments based on m/z ratio, are illustrated in blue, while undetectable but expected intermediates [44,45] are presented in black. These results are in general agreement with previous works that report the generated intermediates during the MB photodegradation process [44,45].



**Figure 11.** Proposed photocatalytic degradation pathway of MB. Detected degradation products are illustrated in blue, while expected but undetectable [44] species are presented in black.

#### 3. Materials and Methods

#### 3.1. Chemicals

All reagents were used without further purification. Chemicals of HPLC grade were acetic acid  $(C_2H_3O_2, Merck, Darmstadt, Germany)$  and acetonitrile  $(C_2H_2N, J.T. Baker, CA, USA)$ . Chemicals of AR grade were ethanol  $(C_2H_5OH, Merck, Germany)$ , potassium bromide (KBr, Merck, Germany), tert-butanol  $(C_4H_{10}O, Merck, Germany)$ , ammonium acetate  $(C_2H_2ONH_4, Rankem, Gurugram, India)$ , sodium hydroxide (NaOH, Rankem, India), methylene blue  $(C_{16}H_{18}N_3Cl, Fluka, Saint Louis, MO, USA)$ , strontium carbonate (SrCO<sub>3</sub>, Fluka, USA), concentrated hydrochloric acid (HCl, Lab Scan, Ireland), mercury(II) sulphate (HgSO<sub>4</sub>, QRëc, Newzaland), nitric acid (HNO<sub>3</sub>, Mallinckrodt Chemicals, Phillipsburg, NJ, USA), potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, Unilab, Mandaluyong, Philippines), potassium hydrogen phthalate (C<sub>8</sub>H<sub>5</sub>KO<sub>4</sub>, Univar, Redmond to Downers Grove, IL, USA), silver sulphate (AgSO<sub>4</sub>, Carlo Erba, Barcelona, Spain), strontium hydroxide octahydrate (Sr(OH)<sub>2</sub>·8H<sub>2</sub>O, Sigma Aldrich, Saint Louis, MO, USA) and concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, Lab supplies, Spain).

## 3.2. Synthesis of Strontium Carbonate (SrCO<sub>3</sub>)

Strontium carbonate (SrCO<sub>3</sub>) was synthesized by a solvothermal method modified from the procedure of Zhang et al. [34]. A suspension of 20 g Sr(OH)<sub>2</sub>·8H<sub>2</sub>O in ethanol (100 mL) was sonicated in an ultrasonic bath for 20 min, followed by solvothermal treatment in an autoclave at 80, 100, 120 or 150 °C for 2 h. The reaction mixtures were left at room temperature to cool down to room temperature. Then, the precipitates were washed with deionized water to remove Sr(OH)<sub>2</sub>·xH<sub>2</sub>O, dried and kept in a dry condition at room temperature. After obtaining the optimal treatment temperature, the reaction time was investigated through the above procedure by fixing the treatment temperature at 100 °C and varying reaction time between 0.5, 1, 2 or 3 h. The strontium-based samples were prepared by varying the Sr(OH)<sub>2</sub>·8H<sub>2</sub>O: ethanol mole ratio as either 1:13, 1:18, 1:23 or 1:27, and then the above procedures were followed using a treatment temperature of 100 °C for 2 h.

#### 3.3. Materials Characterisation

The crystallinity and the phase structure of the samples were investigated using X-ray diffractometry (PXRD, Bruker AXS model D8 advance). The measurements were examined with CuK $\alpha$  radiation between 2 $\theta$  values of 10–80 degrees, at a scan rate of 0.075 degree·min<sup>-1</sup> using accelerating voltage and currents of 40 kV and 40 mA, respectively. Chemical composition and bonding information were probed using Fourier transform infrared spectrophotometry (FT-IR, Elmer model lamda 800). Diffusion reflectance spectra were measured on a UV–VIS spectrophotometer (Agilent Cary 5000) using a scanning rate of 200–1100 nm. Sample morphologies were investigated using scanning electron microscopy (SEM). The thermal decomposition of SrCO<sub>3</sub> was monitored using a thermogravimetric analyzer (TGA, TA instruments SDT 2960 Simultaneous DSC-TGA).

#### 3.4. Catalyst Performance Examinations

SrCO<sub>3</sub> samples were dispersed in 10 mL of 10 ppm MB aqueous solution in order to observe the change in colour under dark and visible light irradiation conditions. Before illumination, the suspensions were stirred in the dark for 5 min. Then, suspensions were irradiated using an LED (16 × 12 V EnduraLED 10 W MR16 dimmable 4000 K with  $\lambda > 400$  nm) [46]. The colour removal efficiency of MB was monitored as a function of degradation time by measuring the absorbance of the dye solution after treatment. In order to terminate the reaction, the photocatalyst was filtered off using a syringe filter (0.45 µm). The absorbance of the dye was then measured, and the concentration of remaining MB was quantified using the absorbance at maximum wavelength (around 664.5 nm) using the Beer Lambert law.

The colour removal efficiency of MB was calculated via Equation (1):

Colour removal efficiency = 
$$\left(\frac{C_0 - C_t}{C_0}\right) \times 10$$
 (1)

where  $C_0$  is the concentration of fresh MB solution, and  $C_t$  is the concentration of dye residue after treatment at *t* minutes.

Leaching of strontium ions may be a major cause of photocatalyst deactivation. Therefore, the amount of strontium ions in the filtered MB solution was quantified by flame atomic absorption spectrometry (FAAS, Perkin Elmer, Waltham, MA, USA).

A mass spectrometer (micro TOF MS, Bruker, Billerica, MA, USA) equipped with electrospray ionization (ESI) source was employed to detect MB degradation products. For this, direct injection of the treated MB solution (with 1:23 SrCO<sub>3</sub>) under visible light irradiation was carried out, with fragments examined over the range m/z 50–700.

## 4. Conclusions

In this work, a solvothermal method without any calcination step was employed to prepare a single crystalline phase of strontium carbonate (SrCO<sub>3</sub>). Ethanol incorporated SrCO<sub>3</sub>, a visible light responsive SrCO<sub>3</sub> material having a bandgap energy of 2.62 eV, was obtained from the solvothermal treatment of hydrated strontium hydroxide in ethanol at Sr:EtOH of 1:23. Nevertheless, the synthesis conditions strongly influence the bandgap energy of SrCO<sub>3</sub>, as UV responsive SrCO<sub>3</sub> material can also be obtained by varying the precursor concentration. The narrow bandgap SrCO<sub>3</sub> material can be utilized as a photocatalyst for decolourisation of methylene blue in water under visible light irradiation. Effective decolourisation of 10 ppm methylene blue aqueous solutions was achieved with >99% colour removal efficiencies after 3 h treatment, under visible light irradiation over the 1:23 photocatalyst, using a catalyst loading of 4 g·L<sup>-1</sup>. The decolourisation is mainly due to photocatalytic processes. The rate constant values showed a direct correlation with temperature, but decolourisation was most rapid at low pH. In addition to the conventional uses of SrCO<sub>3</sub> in pyrotechnics and frit manufacturing, synthesized SrCO<sub>3</sub> materials have their place as semiconductors and cocatalysts employed in energy

and environmental applications. The key findings of this work highlight that incorporated ethanol in the  $SrCO_3$  structure results in a narrowing of the energy bandgap in  $SrCO_3$ , with the material being a visible light responsive semiconductor and active photocatalyst in dye degradation. Results from this work may suggest alternative synthesis routes to obtain visible responsive  $SrCO_3$  materials, for further development of new composites and cocatalysts in broader applications.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4344/10/9/1069/s1. Figure S1: PXRD patterns of Sr-containing samples derived from solvothermal treatments of hydrated strontium hydroxide in ethanol (a) at various solvothermal temperatures, 2 h, Sr:EtOH mole ratios of 1:23 and (b) at various solvothermal treatment times, 100 °C, Sr:EtOH mole ratios of 1:23; Figure S2: FTIR spectra of Sr-containing samples derived from solvothermal treatment of hydrated strontium hydroxide in ethanol (a) at various solvothermal treatment of hydrated strontium hydroxide in ethanol (a) at various solvothermal temperatures, 2 h, Sr:EtOH mole ratios of 1:23; Figure S2: FTIR spectra of Sr-containing samples derived from solvothermal treatment of hydrated strontium hydroxide in ethanol (a) at various solvothermal temperatures, 2 h, Sr:EtOH mole ratios of 1:23 and (b) at various solvothermal treatment times, 100 °C, Sr:EtOH mole ratios of 1:23 and (b) at various solvothermal treatment times, 100 °C, Sr:EtOH mole ratios of 1:23.

**Author Contributions:** Formal acquisition, investigation and writing—original draft, P.W. writing—review, editing, T.K.; funding acquisition, writing—review, editing and supervision, S.M.S. All authors have read and agreed to the published version of the manuscript.

**Funding:** M.Sc. Student scholarship (for P.W.) was provided by the Center of Excellence for Innovation in Chemistry (PERCH-CIC). This work was partially supported by the Thailand Research Fund (Grant No. RSA5980027 and IRN62W0005) for T.K. and S.M.S., the National Research Council of Thailand for P.W, and by the CIF, Faculty of Science, Mahidol University.

**Acknowledgments:** The authors are grateful for partial financial support from the Thailand Research Fund (Grant No. RSA5980027 and IRN62W0005), the National Research Council of Thailand, and the CIF, Faculty of Science, Mahidol University. PP is thankful for an M.Sc. student scholarship from the Center of Excellence for Innovation in Chemistry (PERCH-CIC).

Conflicts of Interest: The authors declare no conflict of interest.

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