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Microwave-assisted synthesis and enhanced photocatalytic performance of $\text{Bi}_2\text{O}_2\text{CO}_3$ nanoplates

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Abstract

In this research, $\text{Bi}_2\text{O}_2\text{CO}_3$ (BOC) nanoplates as a semiconductor-based photocatalyst composed of $[\text{Bi}_2\text{O}_2]^{2+}$ configuration layers were used for environmental treatment. Highly crystalline and pure phase of BOC nanoplates were successfully synthesized by a microwave-assisted method. Effect of irradiation time and microwave heating power on phase, purity, crystallinity, particle size and morphology of the as-synthesized products was investigated. The as-synthesized BOC nanoplates were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), dynamic light scattering (DLS) spectroscopy, Brunauer-Emmett-Teller (BET) surface area analysis, photoluminescence (PL) spectroscopy and UV-visible spectroscopy. Upon increasing microwave heating power, purity and crystallinity of the as-synthesized products were improved. Due to the existence of double internal electric field, the separation of photo-induced charged carriers was enhanced, leading to promote photocatalytic activity of the BOC nanoplates in degrading of methyl orange (MO) under UV radiation. The highest photocatalytic performance was achieved by

using the BOC nanoplates synthesized by 600 W microwave for 60 min. A formation mechanism of BOC nanoplates was also proposed and discussed according to the experimental results.

Keywords: $\text{Bi}_2\text{O}_2\text{CO}_3$ nanoplates; Photocatalysis; Spectroscopy; X-ray diffraction

1. Introduction

Semiconductor-based photocatalysts are considered as promising materials in purification and disintegration of pollutants containing in wastewater, remedy for hazardous waste and wastewater treatment as compared with traditional strategies [1-6]. They are harmless to surrounding environment and can be used to degrade organic pollutants to non-hazardous products through photo-induced oxidation reaction [1-6]. However, the properties of conventional semiconductor photocatalysts are severely limited by several factors: low utilization of visible-light and fast recombination of photogenerated charge carriers [4-9]. The crystalline structure and surface of semiconducting materials are able to play the role in their physical and chemical properties [1, 4, 6, 9, 11]. Thus, many efforts have been devoted to modify semiconductors and to explore for new UV-visible light responsive photocatalysts. Among the investigated photocatalysts, bismuth-based semiconductors, particularly Sillén-type structure BiOX ($X = \text{Cl}, \text{Br}, \text{I}$) [1-4], Aurivillius structure Bi_2XO_6 ($X = \text{W}, \text{Mo}$) [5-10], Sillén-structure-related $\text{Bi}_2\text{O}_2[\text{BO}_2(\text{OH})]$ [11-13] and $\text{Bi}_2\text{O}_2(\text{OH})(\text{NO}_3)$ [14] have been intensively studied due to their unusual layered structure, adequate chemical stability and superior photocatalytic performance. These materials are composed of $[\text{Bi}_2\text{O}_2]^{2+}$ fluorite structure layers and interleaved halide ions, perovskite-like $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2+}$ or $\text{BO}_3^{3-}/\text{NO}_3^-$ ionic blocks, which can induce strong internal static electric field. Consequently, the separation of electron-hole pairs and diffusion of photoinduced charges are promoted. Comparing to bulk photocatalysts without layered structure, the layered structure photocatalysts are more favorable environment for diffusion and separation of photoexcited electron-photoinduced hole pairs because the oxidation and reduction sites exist on the surfaces and edges of the sheet units. Holes generated in the layered photocatalysts diffuse to a very short distance before reaching the surface of the sheet units. They can be trapped by interlayer water molecules. The rapid hole-trapping process allows electrons to freely and sufficiently diffuse through the sheet units until reaching the sheet edges. Recently, the $[\text{Bi}_2\text{O}_2]^{2+}$ fluorite-structure attributes a number of oxygen vacancies [12],

which can lead to extend the wavelength coverage of light response. $\text{Bi}_2\text{O}_2\text{CO}_3$ (BOC) is a unique Bi-based semiconductor with Aurivillius/Sillen-related structure layer which is composed of alternating $[\text{Bi}_2\text{O}_2]^{2+}$ sheets and CO_3^{2-} anions [15-17].

The BOC nanostructures are semiconductors with great potentials for different applications: microelectrodes [18], humidity sensors [19-20], supercapacitors [21-22], anti-bacterial performance [23] and photocatalysts [15-17, 24-31]. Due to the non-toxicity, environment-friendly and good chemical stability properties, the materials have attracted much attention to a number of researchers. These properties are largely controlled by temperature, particle size, morphology and synthetic method [29]. Recently, versatile structure of BOC including nanorods, nanoflowers and nanowires has been extensively studied to obtain unique properties and investigate for future application. Upon pursuing the nanostructure, different chemical and physical methods have been developed to synthesize nanostructure BOC materials: solvothermal route [24], hydrothermal synthesis [15-17, 24-30], template assisted synthesis [31] and co-precipitation [32]. These methods are quite expensive and complicate, long reaction time consuming, high energy consumption, template requirement and contaminated products with difficulty in economic efficiency for practical applications. To solve the above problems, microwave-assisted synthesis is a good approach. It is an efficient, energy saving and environmentally friendly process for the synthesis of inorganic nanomaterials with different morphologies. Microwave is a good method used to generate interaction between chemicals occupying electric charges in order to create internal heat during the proceed reaction. The resulting volumetric heating can lead to homogeneous nucleation, high reproducibility and well-defined particle size with narrow size distribution. Moreover, it is much rapid process, shorter crystallization time, high yield product by decreasing the formation of impurities during the reaction and enhancing the reaction rate comparing with other conventional heating method [33-37].

In the present study, the effect of irradiation time and microwave power on the morphology and optical properties of BOC nanostructure obtained by a microwave-assisted aqueous solution method was studied. The as-synthesized products were characterized by different techniques to determine phase, morphology, crystallite size, atomic vibration and optical properties. The best semiconducting materials were used for photocatalytic process in order to decompose organic pollutants induced by UV light. The photocatalytic performance of BOC photocatalysts was evaluated

through the decomposition of methyl orange (MO) under UV light irradiation. In addition, a possible mechanism for photodegradation of organic pollutants by BOC photocatalysts was proposed.

2. Experimental method

2.1 Preparation of $\text{Bi}_2\text{O}_2\text{CO}_3$ nanostructure

The $\text{Bi}_2\text{O}_2\text{CO}_3$ (BOC) nanoplates were synthesized by a microwave assisted synthesis method. All the reagents used in the experiment were analytical-grade and were used without any further purification. In a typical synthetic procedure, 4.8507 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was first dissolved in 10 ml of 1 M HNO_3 , labeled as solution A. Concurrently, 8.4792 g of Na_2CO_3 was dissolved in 90 ml deionized water, labeled as solution B. When the above solutions were clear, the solution B was dropped into solution A with 30 min stirring and plenty of white precipitates formed. Then, the whole system was processed at different synthetic conditions by varying of microwave power from 100 W to 600 W and irradiation time of 15-60 min. In the end, the as-synthesized products formed, and were washed with deionized water and ethanol three times to remove some residual reactants. The final products were dried in air at 70 °C for 12 h for further characterization.

2.2 Characterization

The as-synthesized products were characterized by different techniques to identify phase, morphology, structure and constituent. Phase of the samples was characterized by an X-ray diffractometer (Rigaku SmartLab XRD) operating at 20 kV, 15 mA with $\text{Cu K}\alpha$ radiation (0.15405 nm) at a scanning rate of 0.02 °C/s in the 2θ range of 10–60 deg. Atomic vibration of the BOC was analyzed by Fourier transform infrared spectroscopy (FTIR, Bruker Tensor 27) with KBr as a diluting agent operating in the range of 4000–400 cm^{-1} . The morphology of the samples was examined by a field-emission scanning electron microscope (SEM, JEOL JSM-6335F) and a transmission electron microscope (TEM, JEOL JEM-2010). Energy-dispersive X-ray (EDX) spectroscopy was used in conjunction with the SEM analyzer used to characterize the elemental composition of the sample. The particle size distribution was examined by dynamic light scattering (DLS, Malvern Instruments Zetasizer Nano-S). The specific surface area was measured on a Nova surface area analyzer (Quantachrome Instruments) by nitrogen adsorption through the Brunauer-Emmett-Teller (BET) method. Ultraviolet visible spectra were recorded on UV-visible spectrophotometer (Thermo Scientific Evolution 201). Photoluminescence (PL)

emission of the products was analyzed by a luminescence spectrophotometer (LS50B Perkin Elmer) in the wavelength range of 300-700 nm with an excitation wavelength of 325 nm.

2.3 Photocatalysis

The photocatalytic activities of $\text{Bi}_2\text{O}_2\text{CO}_3$ were evaluated through the degradation of methyl orange (MO, $\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$) dye under stimulated UV radiation of two 15 W UV lamps. In a typical experiment, each 150 mg of powder photocatalyst was first dispersed in 150 ml of MO dye solution (1.0×10^{-5} M). Before illumination, the suspension was magnetically stirred in the dark for 30 min to establish adsorption-desorption equilibrium between catalyst and organic dye. Then, the suspension was exposed with UV light for different lengths of time until 120 min completion. At a given time interval, about 5 ml of suspension was taken and centrifuged at 7,000 rpm for 10 min to remove the solid photocatalyst. The MO content in the filtrate was determined by a UV-visible spectrophotometer at a maximum absorption of approximately 464 nm. To ensure the reproducibility, duplicate runs were performed to obtain average value at each condition. In this research, absorption intensities were assumed to be in linear proportion with the concentration of MO. The decolorization efficiency (%) was calculated by

$$\text{Decolorization efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

C_0 is the initial dye concentration and C is the dye concentration after photocatalytic test for a period of time (t).

3. Results and discussion

3.1 Phase and chemical analyses

Crystalline structures of the as-prepared samples were examined by X-ray diffraction. XRD patterns of the as-synthesized BOC samples at different microwave exposure lengths of time and microwave heating powers are shown in Figures 1 and 2. All the diffraction peaks can be indexed to the tetragonal phase of $\text{Bi}_2\text{O}_2\text{CO}_3$ with the lattice constant $a = 3.8650 \text{ \AA}$ and $c = 13.6750 \text{ \AA}$, which are in agreement with the typical data of the JCPDS card no. 41-1488. No peaks of other phases were detected, indicating that high-purity BOC products were synthesized by the microwave-assisted method. Upon reducing the lengths of microwave irradiation time from 60 min to 45

min, 30 min and 15 min, the XRD peaks of products were broadened, and the crystalline degree of these pure products was lowered. To save the energy consumption, the power of microwave was gradually reduced step by step from 600 W to 450 W, 300 W, 180 W and 100 W at a constant 60 min of microwave exposure time. The products were still pure BOC phase, but the crystalline degree was lessened. This analysis certified that the increase of microwave power played the role in improving the degree of crystallinity. The higher dielectric loss of water used in the present research can lead to enhance the microwave absorption. The vibrating electric field of the microwave induces a force on the charged particles to vibrate accordingly. The vibration of the reactants promotes the reaction kinetics. Thus, the higher temperature of the reaction is reached and the high reaction rate is subsequently enhanced.

XRD peaks provide information about the X-ray coherence which is close to the average size of a single crystalline domain inside the nanocrystal. The average crystallite size of a sample was calculated using the Scherrer's formula [38],

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

K is a constant (0.94), λ is the wavelength (Cu K_{α} = 0.15405 nm), θ is the Bragg angle and β is the full width at half maximum (FWHM) of the diffraction peak. According to the Scherrer equation, the average crystallite size of the sample was calculated using the (013) peak. The average crystallite size was increased from 19.91 nm to 28.30 nm with the increase of microwave power from 100 W to 600 W. Upon increasing the microwave exposure time from 15 min to 60 min at a constant 600 W, the size of crystallite was also increased.

FTIR spectroscopy was performed to identify functional groups of the as-prepared BOC nanostructure and to determine molecular impurities. The FTIR spectra of the samples prepared under different irradiation conditions are shown in Figures 3 and 4. The bands at 1387 cm^{-1} and 1465 cm^{-1} were assigned to the C=O stretching vibration. The transmittance bands at 551 cm^{-1} and 845 cm^{-1} were attributed to the stretching mode of Bi–O. No spectral absorption for impurities such as NO_3^- was detected, confirming that $\text{Bi}_2\text{O}_2\text{CO}_3$ is pure phase.

3.2 Surface morphology analysis

The SEM images of BOC synthesized by a 600 W microwave power for 15 min, 30 min, 45 min and 60 min are showed in Figure 5. At 600 W microwave and 15 min, the product was incomplete nanoplates. They became complete plates when the length of microwave exposure time was as long as 60 min. By using the length of time of 60 min at different microwave powers (Figure 6), the as-synthesized products with different morphologies were synthesized. Obviously, increasing in the heating power can lead to generate more defined structure with more homogeneous particle size and morphology distribution. At 100 W, the product was composed of a number of nanoparticles clustered together in group. Upon increasing the power of the microwave from 100 W to 180 W, 300 W, 450 W and 600 W, the nanoparticles gradually transformed into incomplete plates at 180 W, 300 W and 450 W and some formed by agglomeration of BOC nanoplates. At 600 W microwave heating, the BOC product was entirely composed of large-scale uniform nanoplates. In this research, both powers of microwave and lengths of time have the influence to control the product morphologies, including their crystalline degrees. The average size of BOC nanoplates was about 200-400 nm and almost unchanged although the reaction time was increased. TEM images and SAED pattern are shown in Figure 7. The results clearly show that the power of microwave can play the role in the shape and size of as-synthesized BOC nanostructure. The average size of nanoplates increased with increasing microwave power from 100 W to 600 W. The selected area electron diffraction (SAED) shows diffraction spot pattern, implying that the as-prepared BOC nanoplate is single crystal.

The atomic composition of as-synthesized BOC nanoplates was determined by EDX as the results shown in Figure 8. The EDX spectrum of BOC nanocrystal revealed the presence of Bi, O and C with Bi:O:C atomic ratio of 2:5:1, in accordance with the $\text{Bi}_2\text{O}_2\text{CO}_3$ chemical formula.

3.3 BET surface area and particle size distribution

The BET specific surface areas of the BOC nanoplates synthesized at different microwave exposure periods and microwave heating powers showed that the BOC sample at 100 W exhibited specific surface area larger than that at 600 W. The morphology and specific surface area of the BOC nanoplates were controlled by microwave power. The surface area of the BOC sample decreases significantly with increasing in the microwave power and the opposite is true for the average grain size.

Dynamic light scattering (DLS) was used to determine the size distribution of particles in solutions. The mean particle sizes were estimated to be 419.49, 369.61, 334.38 and 273.98 nm for as-synthesized BOC nanoplates at 600 W for 60 min, 45 min, 30 min and 15 min, respectively. The BOC nanoplates prepared at 100, 180, 300 and 450 W were uniform nanoplates with narrow particle size distribution. The BOC sample at 600 W shows the highest mean particle size. Upon increasing microwave power, the higher amount of energy is supplied to the reaction medium. This energy is able to readily stimulate nucleation rate, thus resulting in large BOC nanoparticles. These unstable nanoparticles tend to agglomerate and become more stable nanoplates.

3.4 Growth of BOC nanoplates by microwave-assisted method

Based on the experimental results, a formation mechanism of the BOC nanoplates is probably related to the dissociation of $\text{Bi}(\text{NO}_3)_3$ in HNO_3 solution to produce BiONO_3 intermediates. Upon mixing the solution with an aqueous Na_2CO_3 solution, H^+ rapidly reacted with CO_3^{2-} and CO_2 was released. Concurrently, the as-obtained BiONO_3 reacted with excessive CO_3^{2-} ions to form $\text{Bi}_2\text{O}_2\text{CO}_3$ with reduced solubility. A mechanism for the formation of BOC nuclei is as follows.

In this case, a possible formation mechanism of BOC nanoplates by varying microwave irradiation power is shown in Figure 9. In the early stage, the initial BOC nuclei acted as dipoles in the mixture solution under the electric field of microwave. Upon illumination by microwave with different powers, the obtained BOC nuclei polarize and aggregate to form BOC particles. In the next step of reaction, the adjoining nanoparticles grew along the oriented direction, and agglomerated nanoplates formed. The sample processed at 100 W contains irregular plates. The morphology changed to plate-like structure at 180 W, 300 W, 450 W and 600 W. The plate like particles did not completely maintain at 300 W and 450 W comparing to those at 600 W. These plate-like particles formed by stacking of self-assembled spherical nanoparticles in a proper orientation of a particular direction. Significant enhancement of the crystallization was detected with increasing in the applied microwave power and

a little influence of reaction time. High microwave power with high electric field is likely to create more stable nanoplates than low microwave power with low electric field.

3.5 Light absorption, charge separation and photoluminescence

The optical properties of as-prepared BOC nanoplates synthesized by different microwave exposure periods of time and microwave heating powers are shown in Figures 10 and 11. They have similar absorption edges at 200–375 nm. The absorption intensity in UV region of the as-prepared BOC-600 W gradually increased with increasing in the length of time. In addition, the absorbance gradually increased when the microwave power increased from 100 W to 600 W. The BOC at 600 W has the highest light absorption in the UV range. Thus, the BOC at 600 W for microwave exposure time of 60 min has the best photocatalytic activity due to the most effective utilization of photon. Energy band gap (E_g) of as-prepared BOC samples can be determined from the absorbance by the equation.

$$(\alpha hv) = A(hv - E_g)^{n/2} \quad (6)$$

, where α is the absorption coefficient, $h\nu$ is the photon energy, A is a constant and E_g is the energy band gap [39]. Among them, n is controlled by the transition characteristic in a semiconductor: direct transition ($n=1$) or indirect transition ($n=4$). For indirect transition of BOC, n is 4. Thus, the energy band gap (E_g) of the resulting samples can be estimated from the plot of $(\alpha hv)^{1/2}$ versus photon energy ($h\nu$). The intercept of the tangent to the X axis is a good approximation for energy band gap. The calculated energy gaps of the resulting samples were approximately 3.26, 3.24, 3.22 and 3.20 eV for the BOC at 600 W for microwave exposure time of 15 min, 30 min, 45 min and 60 min, respectively. For the BOC nanoplates prepared at 100 W, 180 W, 300 W, 450 W and 600W microwave power, the calculated energy gaps were 3.26, 3.25, 3.25, 3.24 and 3.20 eV, respectively. They can be seen that energy gap of the BOC at 600 W for microwave exposure time of 60 min is the smallest. Furthermore, specific structure, morphology, particle size and defect can play the role in optical absorption and energy gap. Clearly, the BOC at 600 W and exposure time of 60 min has an appropriate energy gap for photocatalytic degradation of organic contaminants under UV light irradiation.

Photoluminescence spectra were investigated to determine the recombination of electron-hole pairs, including the charge separation efficiency. Photoluminescence of the as-synthesized BOC nanoplates synthesized at different microwave exposure

periods and microwave heating powers are shown in Figure 12. For the as-prepared BOC nanoplates at different microwave exposure periods and microwave heating powers, the spectra are very similar in shape. The emission is around 350–600 nm, and BOC 600 W at microwave exposure time of 60 min is the lowest. This suggests that the photogenerated charge carriers with the lowest irradiative recombination and efficient charge separation can be improved by the use of BOC at 600 W and 60 min.

3.6 Photocatalysis

The plate- like BOC samples were used for photocatalytic test. The photocatalytic activities of the as-prepared BOC nanoplates synthesized at different microwave exposure periods and microwave heating powers were measured through the degradation of MO solutions under UV light irradiation. Figure 13 shows the temporal evolution of absorbance during the photocatalytic degradation of MO in the solution containing the BOC nanoplates synthesized at 600 W microwave power for 60 min. The intensity peak at 464 nm corresponding to the MO absorbance gradually decreased with the length of illumination time. The absorbance shows hypsochromic shift because of the demethylated degradation process in a stepwise manner. The BOC sample has good degradation of MO dye which is completely degraded within 120 min.

Figure 14(a) shows photocatalytic performance of the BOC samples synthesized at different microwave exposure periods comparing to the blank test without the catalyst. In the absence of photocatalyst, less than 5 % MO was decolorized by self-photodegradation. The final photodegradation efficiencies of MO were 87.98 %, 89.51 %, 91.63 % and 98.14 % by BOC 15 min, BOC 30 min, BOC 45 min and BOC 60 min within 120 min irradiation, respectively. The degradation rate can be described by the pseudo-first-order kinetics expressed as follows [40].

$$\ln(C_0/C) = kt \quad (7)$$

C_0 is the initial concentration of MO solution, C is the MO concentration within the irradiation time (t) and the slope k is the apparent reaction rate constant [40]. The first-order kinetic plots for MO degradation photocatalyzed by the BOC samples synthesized at different microwave exposure periods are shown in Figure 14(b). The plots correspond to the linear relationship between $\ln(C_0/C)$ and irradiation time. The estimated apparent degradation rate constants were calculated to be 0.0148 min^{-1} , 0.0163 min^{-1} , 0.0180 min^{-1} and 0.0294 min^{-1} by BOC 15 min, BOC 30 min, BOC 45

min and BOC 60 min, respectively. In contrast, the k rate constant of the blank was only 0.0005 min^{-1} .

Figure 15 shows the MO photodegradation by BOC catalysts synthesized at different microwave heating powers and UV irradiation periods. Obviously, BOC sample at 600 W exhibited the highest degradation efficiency of 98.14 % within 120 min irradiation, while BOC at 450 W, 300 W, 180 W and 100 W showed 93.31 %, 89.06 %, 85.57 % and 77.04 % degradation of MO, respectively. The pseudo-first order rate constant for the BOC 100 W, BOC 180 W, BOC 300 W, BOC 450 W and BOC 600 W were 0.0113 min^{-1} , 0.0161 min^{-1} , 0.0165 min^{-1} , 0.0217 min^{-1} and 0.0294 min^{-1} , respectively. Possibly, the photocatalytic performance was due to the particular layer structure. The strong internal static electric field normal to $[\text{Bi}_2\text{O}_2]^{2+}$ and CO_3^{2-} layers is able to promote the separation of electron-hole pairs. The improvement of photocatalytic performance of BOC sample is most likely due to the high crystallinity, small size and large surface area.

Possible radicals for photodegradation of MO over the BOC photocatalyst under stimulated UV light irradiation were investigated by using different radical scavengers: benzoquinone (BQ), isopropyl alcohol (IPA) and disodium ethylenediaminetetraacetate (EDTA) for scavenging the reactive species of $\cdot\text{O}_2^-$, $\cdot\text{OH}$ and h^+ , respectively. Prior to light irradiation, these 1.0 mM scavengers were introduced into MO aqueous solution along with the BOC nanoplates. Based on the addition of BQ, IPA and EDTA, the degradation efficiency of MO (Figure 16) decreases from 98.14 % to 12.73 %, 98.19% to 87.13 % and from 98.14 % to 24.66 %, respectively. The dye without a scavenger showed the greatest degradation. Upon adding with scavengers for $\cdot\text{O}_2^-$ and h^+ , the degradation was dramatically suppressed. Meanwhile, the scavenger for $\cdot\text{OH}$ radicals show no significant suppression. These results indicate that the $\cdot\text{O}_2^-$ and h^+ species were generated during UV light irradiation and played an important role in dye degradation. Moreover, the present experimental results confirmed that $\cdot\text{OH}$ radicals were not the main active species in this system. Clearly, $\cdot\text{O}_2^-$ and h^+ directly degraded MO molecules adsorbed on the BOC nanoplates. The photocatalytic mechanism of the present process stimulated by UV light is as follows.

Based on the above experimental results, a mechanism for MO photocatalytic degradation by BOC nanoplates is proposed (Figure 17). During photocatalytic reaction, charge separation is significant and necessary to prevent recombination of the photoexcited electrons and photoinduced holes. The crystalline structure of BOC with layered configuration is very beneficial for the high photocatalytic performance. Upon UV light irradiation, photoexcited electrons and photoinduced holes were generated on the BOC. The electrons combined with adsorbed O_2 to form $\cdot O_2^-$ radical. Concurrently, the photogenerated holes diffused to the $[Bi_2O_2]^{2+}$ layer and subsequently oxidized OH^-/H_2O to form $\cdot OH$ radical. The inherent orbital distribution leads to effective separation of electron-hole pairs and generation of abundant active species to decompose contaminants. The crystalline structure of BOC is composed of $[Bi_2O_2]^{2+}$ and CO_3^{2-} layers along the [001] direction. The electrostatic field derived from the layered structure and the (001) active facet of BOC are further beneficial to the separation of charge carriers.

3.7 Recyclability of BOC nanoplates

It is well acknowledge that heterogeneous catalysts are superior to the recyclability and stability process. During the photocatalytic process, photo-corrosion of catalysts can lead to significant decrease activity or even complete loss of catalytic activity. Thus, the photostability of the BOC samples was investigated using the degradation of MO as a probe reaction. Aqueous MO with initial concentration of 1.0×10^{-5} M was almost completely removed in each run and there is no obvious decrease in activity after the end of cycle five (Figure 18). The final catalyst collected by centrifugation was characterized by XRD and FTIR which demonstrate no significant change in BOC structure (Figure 19). The results confirm that the BOC nanoplates show high photostability and have good potential in wastewater treatment.

4. Conclusions

A simple, fast, cost effective microwave-assisted aqueous solution method was used to synthesize BOC nanostructure with high crystallinity and purity. They were found that effect of microwave power and microwave heating time played the role in both morphology and crystallinity of the BOC nanostructure. A possible formation mechanism of the BOC nanoplates was proposed based on the interaction of microwave with materials. In this research, the BOC sample prepared at 600 W microwave for 60 min has the highest photodegradation of MO.

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Figure captions

Figure 1. XRD patterns of BOC synthesized by 600 W microwave for 15 min, 30 min, 45 min and 60 min.

Figure 2. XRD patterns of BOC synthesized at 100 W, 180 W, 300 W, 450 W and 600 W for 60 min.

Figure 3. FTIR spectra of BOC synthesized by 600 W microwave for 15 min, 30 min, 45 min and 60 min.

Figure 4. FTIR spectra of BOC synthesized at 100 W, 180 W, 300 W, 450 W and 600 W for 60 min.

Figure 5. SEM images of BOC synthesized by 600 W microwave for (a-d) 15 min, 30 min, 45 min and 60 min, respectively.

Figure 6. SEM images of BOC synthesized by (a-e) 100 W, 180 W, 300 W, 450 W and 600 W for 60 min, respectively.

Figure 7. TEM images of BOC synthesized by (a-e) 100 W, 180 W, 300 W, 450 W and 600 W for 60 min, respectively. (f) SAED pattern of BOC synthesized by 600 W microwave for 60 min.

Figure 8. EDX spectrum of the BOC nanoplates synthesized at 600 W for 60 min.

Figure 9. Schematic diagram for formation of BOC nanoplates synthesized by microwave-assisted method.

Figure 10. (a) UV-vis diffuse reflectance spectra and (b) the plots for $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) of the BOC synthesized by 600 W microwave for different lengths of time.

Figure 11. (a) UV-vis diffuse reflectance spectra and (b) the plots for $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) of the BOC synthesized by different microwave powers for 60 min.

Figure 12. Photoluminescence of the BOC nanoplates synthesized by (a) different lengths of time and (b) different microwave heating powers.

Figure 13. UV-visible absorption of methyl orange photocatalyzed by the BOC nanoplates synthesized at 600 W microwave for 60 min.

Figure 14. (a) Decolorization efficiencies and (b) pseudo-first-order plots for photodegradation of MO by the BOC nanoplates synthesized for 15 min, 30 min, 45 min and 60 min w.r.t. the blank within 120 min.

Figure 15. (a) Decolorization efficiencies and (b) pseudo-first-order plots for photodegradation of MO by the BOC nanoplates synthesized by 100 W, 180 W, 300 W, 450 W and 600 W w.r.t. the blank within 120 min.

Figure 16. Effect of different scavengers on photodegradation of MO over the BOC nanoplates synthesized by 600 W microwave for 60 min under UV light irradiation.

Figure 17. Schematic diagram for photocatalysis of the BOC nanoplates under UV radiation.

Figure 18. Repeated photodegradation curves of MO over the BOC nanoplates for five cycles.

Figure 19. (a) XRD pattern and (b) FTIR spectrum of the re-used BOC at the end of cycle five.

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Figures

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