Facile Cetyltrimethylammonium Bromide (CTAB)-assisted Synthesis of Calcium Bismuthate Nanoflakes with Solar Light Photocatalytic Performance

Zi Wang¹, Hongjun Chen¹, Fanglv Qiu¹, Zeyang Xue¹, Chunhu Yu¹, Pengxiang Wang¹, Qianmin Cong¹, Lizhai Pei¹,²,*, Chuangang Fan¹,²,* and Yong Zhang³

¹School of Materials Science and Engineering, Anhui University of Technology, Ma’anshan, Anhui 243002, P.R. China; ²Key Laboratory of Metallurgical Emission Reduction & Resources Recycling, Ministry of Education, Anhui University of Technology, Ma’anshan, Anhui 243002, P.R. China; ³The Key Laboratory for Power Metallurgy Technology and Advanced Materials of Xiamen, Xiamen University of Technology, Xiamen, Fujian 361024, P.R. China

Abstract: Background: Wastewater with dyes pollutes the environment and causes serious risk to human health and aquatic biota. Gentian violet (GV) belongs to typical triphenylmethane dyes and is difficult to be degraded. Calcium bismuthate nanoflakes possess good photocatalytic activity toward GV under solar light irradiation.

Objective: The aim of the study was to prepare calcium bismuthate nanoflakes by the hydrothermal method and research on the solar light photocatalytic performance of the calcium bismuthate nanoflakes for GV degradation.

Methods: Calcium bismuthate nanoflakes were synthesized via a facile hydrothermal route assisted by cetyltrimethylammonium bromide (CTAB) based on the reaction of sodium bismuthate and calcium chloride. The calcium bismuthate products were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy and solid UV-vis diffuse reflectance spectrum.

Results: The calcium bismuthate nanoflakes possess single crystalline monoclinic CaBi₂O₄ phase. The size of the whole nanoflakes is about 10 μm and the thickness of the nanoflakes is about 40 nm. The morphology, size and phase of the products are closely relative to CTAB concentration, reaction temperature and reaction time. The bandgap of the calcium bismuthate nanoflakes is 2.21 eV. The photocatalytic activity of the calcium bismuthate nanoflakes is high enough to completely degrade GV under solar light irradiation for 6 h.

Conclusion: The photocatalytic performance for the removal of GV is dependent on the irradiation time, dosage of the calcium bismuthate nanoflakes and initial GV concentration. The calcium bismuthate nanoflakes exhibit great promising activity for the removal of organic pollutants.

Keywords: Calcium bismuthate nanoflakes, cetyltrimethylammonium bromide, electron microscopy, gentian violet, solar light, photocatalysis.

1. INTRODUCTION

Dyes are widely used in different industry fields, such as leather tanning, hair coloring, textile industry, plastics and paper production which generate a large amount of wastewater [1-4]. Dyes are toxic substances and stable for a long time [5, 6]. Wastewater with dyes pollutes the environment and causes serious risk to human health and aquatic biota [7-11]. Gentian violet (GV) belongs to typical triphenylmethane dyes and is difficult to be degraded [12]. Nanotechnology exhibits great applications in modern science [13-20]. Adsorptive removal method has been developed for the removal of GV using the adsorbents, such as CoFe₂O₄/activated carbon magnetic composite [21], bentonite [22] and succinylated sugarcane bagasse [23]. However, GV can only be removed by transferring GV molecules to absorbents. Photocatalytic method is an effective technology for GV degradation using titanium dioxide in the presence of UV light and oxygen [24]. Electron and hole pairs are considered to be
formed from the interlayer space of the photocatalysts by the photo-absorption process. The relevant reactions can be expressed as follows (Eqs. 1-3) [25]:

\[
\text{Photocatalysts} + h\nu \rightarrow e^- + h^+ \quad (1)
\]

\[
h^+ + H_2O \rightarrow \cdotOH + H^+ \quad (2)
\]

\[
h^+ + \cdotOH \rightarrow \cdotOH \quad (3)
\]

However, titanium dioxide possesses a large bandgap and can only degrade GV under UV light irradiation. It is facile to remove GV under solar slight irradiation using visible light photocatalysts. Therefore, it is essential to explore new visible light photocatalysts to remove GV. The approach for developing efficient photocatalysts is the integration of the biomimetic and bioinspiration to design novel sunlight-driven materials which can improve the light trapping and pollutant adsorption [26-30]. Novel and efficient photocatalysts developed by different methods show great application potential for water decontamination [31-42].

Bismuth-containing nanoscale materials exhibit great application potential in various fields [43-48], especially in the field of the photocatalytic treatment of organic pollutants under visible light [49-54]. Among these bismuth-containing nanoscale materials, bismuthate-based nanoscale materials show special potential for the application of the treatment of organic pollutants owing to the low bandgap, strong visible light, absorption ability and large specific surface area [55-57]. Calcium bismuthate nanoscale materials belong to typical bismuthate-based nanoscale materials which possess low bandgap and good photocatalytic activity for the removal of organic pollutants. For example, Shtarev et al. [58] reported the synthesis of the calcium bismuthate nanoscale particles with rhombohedral, orthorhombic structure and bandgap of 2.47 eV. The calcium bismuthate nanoscale particles showed good photocatalytic activity toward methylene blue under visible light irradiation. The performance of the nanoscale materials is relative to the morphology. Therefore, it is interesting to synthesize calcium bismuthate nanoscale materials with different morphologies, such as calcium bismuthate nanoflakes, exploring possible novel performance. Compared with the existing works, the calcium bismuthate nanoflakes are expected to possess better photocatalytic performance.

Hydrothermal route is a kind of facile method for synthesizing nanoscale materials with different morphologies [59-65]. Cetyltrimethylammonium bromide (CTAB) is an efficient surfactant in the hydrothermal system for inducing the formation of the nanoflakes with various compositions [66-69]. To date, no calcium bismuthate nanoflakes by the hydrothermal route with or without CTAB have been reported. Herein, a facile hydrothermal route assisted by CTAB has been used for the preparation of the calcium bismuthate nanoflakes. The formation process of the calcium bismuthate nanoflakes has also been analyzed by controlling the hydrothermal temperature, reaction time and CTAB concentration. The photocatalytic performance of the calcium bismuthate nanoflakes for the removal of GV is also investigated in detail.

2. MATERIALS AND METHODS

2.1. Materials

All chemical reagents were of analytical grade and used during the experimental process. Sodium bismuthate (purity: ≥99.7%) and GV (purity: ≥99.7%) were obtained from Sinopharm Chemical Reagent Co., Ltd. of P. R. China. Calcium chloride (purity: ≥99.7%) was purchased from Tianjin Zhiyuan Chemical Reagents Co., Ltd. of P.R. China. CTAB (purity: ≥99.7%) was purchased from Anhui Super Chemical Technology Co., Ltd. of P.R. China.

2.2. Synthesis of Calcium Bismuthate Nanoflakes

In a typical synthesis process, CTAB with different concentrations was used as the surfactant and added into 60 mL mixed aqueous solution with sodium bismuthate and calcium chloride under strong stirring at room temperature for 30 min. The mole ratio of sodium bismuthate and calcium chloride was 1:1. The mass ratio of CTAB and water was 1% to 5%. Then the mixed solution was put into a 100 mL Teflon-lined autoclave. The autoclave was maintained at 80°C to 180°C for 0.5 h to 24 h, and then cooled to room temperature naturally. The white precipitate was collected, washed with distilled water, alcohol and acetone for several times, respectively and dried in air at 60°C for 24 h. Series of white calcium bismuthate products were gained by controlling the hydrothermal temperature, reaction time and CTAB concentration to analyze the formation process of the calcium bismuthate nanoflakes.

2.3. Characterization

The phases of the calcium bismuthate products were analyzed by using a Bruker AXS D8 X-ray diffractometer with a graphite monochromatized Cu-Kα radiation and 20 range of 20° – 80°. The morphologies of the calcium bismuthate products were measured using scanning electron microscopy (SEM, JEOL JSM-6490LV, Japan) and transmission electron microscopy (TEM, JEOL JEM-3010, Japan). TEM sample was prepared by dipping the suspension solution in calcium bismuthate nanoflakes after the calcium bismuthate nanoflakes were dispersed in the ethanol solution with ultrasonic stirring for 30 min. Solid UV-vis diffusion reflectance spectrum of the calcium bismuthate nanoflakes was collected by using UV3600 UV-vis spectrometer (Shimadzu International Co., Ltd., Japan) with the integrating sphere. Barium sulfate powder was used as the reference sample. Tauc plot method was applied for determining the bandgap of the calcium bismuthate nanoflakes [41]. The specific surface area of the calcium bismuthate nanoflakes was measured by Brunauer-Emmet-Teller (BET) method using a Micromeritics Gemini VII2390 apparatus (Micromeritics, Norcross, GA) with nitrogen adsorption at 77 K. Prior to adsorption, the calcium bismuthate nanoflakes were purged in He gas atmosphere at 473 K for 1 h.

2.4. Photocatalytic Experiments

The photocatalytic activity of the calcium bismuthate nanoflakes obtained at 180°C for 24 h with 5wt.% CTAB
Calcium Bismuthate Nanoflakes with Good Solar Light Photocatalytic Performance was analyzed according to the photo-degradation of GV. The photocatalytic experiments were conducted at room temperature with the pH value of 7. 2.5-20 mg calcium bismuthate nanoflakes were added into 10 mL 10 mg·L⁻¹ GV aqueous solution with the ultra-sonication, followed by stirring in the dark to reach adsorption-desorption equilibrium between the calcium bismuthate nanoflakes and GV molecules. The photocatalytic treatment process was performed by stirring the mixture of calcium bismuthate nanoflakes and GV under natural solar light irradiation. The GV suspension solution was withdrawn at the given time interval. After the centrifugation, the residual GV solution was measured by the UV756 UV-vis spectrophotometer (Shanghai Youke Instrument Co., Ltd., P.R. China). The reusability of the calcium bismuthate nanoflakes for the photocatalytic degradation of GV was evaluated over six cycles of reuse under natural solar light. The total organic carbon (TOC) was measured by a TA-1.0 TOC analyzer (Neuronbc, P.R. China).

3. RESULTS AND DISCUSSION

3.1. Structure and Morphology of the Calcium Bismuthate Nanoflakes

Fig. (1) shows the XRD pattern of the calcium bismuthate nanoflakes obtained by using the hydrothermal method under the conditions of 180°C for 24 h with 5wt.% CTAB. The strong diffraction peaks suggest that the calcium bismuthate nanoflakes are composed of a good crystalline structure. All diffraction peaks contribute to monoclinic CaBi₂O₄ phase (JCPDS PDF card, No. 48-0216). The monoclinic CaBi₂O₄ phase is different from that reported by Shtarev et al. [58]. No other phases are formed in the calcium bismuthate products besides the monoclinic CaBi₂O₄ phase suggesting that the products consist of a pure monoclinic CaBi₂O₄ phase.

Micro-morphology, size and structure of the calcium bismuthate nanoflakes were analyzed by SEM, TEM and HRTEM observations. Fig. (2a) shows the SEM images with different magnifications of the calcium bismuthate nanoflakes obtained at 180°C for 24 h with 5wt.% CTAB. As shown in Fig. (2a), the obtained products are composed of two-dimensional flake-like crystals. The size of the whole nanoflakes is about 10 μm. The magnified SEM image (Fig. 2b) shows that the calcium bismuthate nanoflakes have a thickness of about 40 nm. The nanoflake-like morphology is similar to that reported by other groups [70-74]. TEM image (Fig. 3a) shows a typical nanoflake-like morphology which is similar to that by SEM observation. The size of the nanoflakes is smaller than that observed by SEM which originates from the fracture of the nanoflakes during the ultrasonic treatment process for the preparation of the TEM sample. The calcium bismuthate nanoflakes are longer than 6 μm. HRTEM image (Fig. 3b) shows that the nanoflakes have clear and regular crystalline lattices. The space of the crystalline lattice is about 0.88 nm which corresponds to {111} plane of monoclinic CaBi₂O₄ phase. The result shows that the calcium bismuthate nanoflakes are composed of single crystalline monoclinic CaBi₂O₄ structure.
3.2. Influence of the Growth Conditions on the Formation of the Calcium Bismuthate Nanoflakes

A series of experiments under different hydrothermal conditions were carried out in order to explore the possible formation process of the calcium bismuthate nanoflakes. It was reported that the CTAB, as a kind of surfactant, plays an essential role in the formation of the nanoscale materials with special morphologies [75-77]. Therefore, several experiments controlling different mass ratios of the CTAB added in the hydrothermal system were firstly conducted to analyze the role of the CTAB concentration in the structure and morphology evolution of the products. The hydrothermal temperature and reaction time were determined as 180 °C for 24 h. The CTAB concentration in the hydrothermal solution was 0 to 5wt.%. The SEM images of the products are shown in Fig. (4). The products obtained without CTAB are shown in Fig. (4a and b). Clearly, only microscale particles with a size of 500 nm–5 μm can be detected in the products. No nanoflake-like morphology is found. When a small amount of CTAB with the concentration of 1wt.% was added into the hydrothermal solution, some nanoflake-like products were observed besides irregular particles of microscale and nanoscale size (Fig. 4c and d). Further increasing the CTAB concentration to 3wt.% caused the formation of the nanoflakes (Fig. 4e and f). The nanoflakes have the size of several micrometers. The thickness of the nanoflakes is about 300 nm. The result of the work confirms that the CTAB has an essential role in the formation of the calcium bismuthate nanoflakes. The adsorption of the CTAB molecules to the surface of the facets of the calcium bismuthate significantly lowers the free energy inducing the formation of calcium bismuthate nanoflakes. A similar phenomenon was also observed for the synthesis of the Zn2GeO4 nanoflakes [66] and silver nanoflakes [78]. Increasing CTAB concentration to 5wt.%, the thickness of the nanoflakes decreased to about 40 nm. To further understand the phase evolution of the products, the XRD patterns of the products obtained from different CTAB concentrations were measured as shown in Fig. (5). It is obvious that the phases of the products obtained from different CTAB concentrations are similar. The products are mainly composed of monoclinic CaBi2O4 phase and a small amount of residue triclinic Bi2O3 phase (JCPDS PDF card, No. 50-1088). The intensity of the diffraction peaks of the triclinic Bi2O3 phase decreases obviously with increasing CTAB concentration. The calcium bismuthate nanoflakes with pure monoclinic CaBi2O4 phase and thickness of about 40 nm can be obtained using 5wt.% CTAB. Therefore, 5wt.% is chosen as the optimal CTAB concentration in this research.

Fig. (3). Transmission electron microscopy images of the calcium bismuthate nanoflakes obtained at 180 °C for 24 h using 5wt.% CTAB. (a) TEM, (b) HRTEM. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

Fig. (4). SEM images of the products obtained at 180 °C for 24 h using different CTAB concentrations. (a) and (b) Without CTAB, (c) and (d) 1wt.% CTAB, (e) and (f) 3wt.% (A higher resolution / colour version of this figure is available in the electronic copy of the article).
Calcium Bismuthate Nanoflakes with Good Solar Light Photocatalytic Performance

Current Nanoscience, 2021, Vol. 17, No. 2

The morphologies of the products are also sensitive to the temperature and reaction time of the hydrothermal reaction process. To substantially understand the role of the hydrothermal temperature in the morphology of the products, the experiments using different reaction temperatures with the reaction time of 24 h adding 5wt.% CTAB were carried out. The products obtained at 80°C were composed of irregular particles with a size of less than 300 nm (Fig. 6a and b). As the reaction temperature increased to 120°C, the obtained products still contained a large amount of irregular particles. And some flake-shaped products with a size of about 2 μm were also formed (Fig. 6c and d). These particles are considered to work as the seeds for the formation of calcium bismuthate nanoflakes. Fig. (7) shows the phase evolution of the products obtained from different reaction temperatures. The products obtained from different reaction temperatures are composed of monoclinic CaBi₂O₄ and triclinic Bi₂O₃ phases. Especially, the intensity of the diffraction peaks of the monoclinic CaBi₂O₄ phase increases obviously with reaction temperature increasing from 80°C to 120°C. At the same time, the intensity of the diffraction peaks of the residue triclinic Bi₂O₃ phase decreases sharply; even some diffraction peaks disappear. The reaction temperature-dependent results show that the hydrothermal temperature promotes the hydrothermal reaction between sodium bismuthate and calcium chloride. The formation of the calcium bismuthate nanoflakes is closely relative to the reaction temperature.

Fig. (5). XRD patterns of the products obtained at 180 °C for 24 h using different CTAB concentrations. (a) Without CTAB, (b) 1wt.%, (c) 3wt.%. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

Fig. (6). SEM images of the products obtained at various temperatures for 24 h using 5wt.% CTAB. (a) and (b) 80 °C, (c) and (d) 120 °C. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

Fig. (7). XRD patterns of the products obtained at various reaction temperatures for 24 h using 5wt.% CTAB. (a) 80 °C, (b) 120 °C. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

A series of products at different time intervals at 180°C adding 5wt.% CTAB were collected to investigate the role of the reaction time in the morphology and phase evolution of the calcium bismuthate nanoflakes. Fig. (8) shows the SEM images with different magnifications of the calcium bismuthate products obtained from different time intervals. It is observed that a large amount of calcium bismuthate nanoflakes are formed at the initial reaction stage (0.5 h at 180°C) (Fig. 8a and b). The calcium bismuthate nanoflakes have a length less than 2 μm and thickness of about 20 nm, respectively. Besides calcium bismuthate nanoflakes, some nanoscale particles with a size of less than 100 nm still exist in the products. As the reaction time increases from 0.5 h to 12 h, the length and thickness of the calcium bismuthate nanoflakes increase to about 8 μm and 30 nm, respectively (Fig. 8c and d). Obviously, the amount of the nanoscale particles decreases. The result indicates that longer reaction time is the main factor leading to further growth in the length and thickness direction of the calcium bismuthate nanoflakes. Fig. (9) shows the XRD patterns of the products from different time intervals. Similar to those obtained from different reaction temperatures, the products are comprised of monoclinic CaBi₂O₄ and triclinic Bi₂O₃ phases. With increasing the hydrothermal reaction time from 0.5 h to 12 h at 180°C, the intensity of the diffraction peaks of the monoclinic
CaBi₂O₄ phase increases obviously. The diffraction peaks of the residue triclinic Bi₂O₃ phase including 2θ = 23.9°, 51.3° and 71.4° disappear. The reaction time obviously promotes the formation of the calcium bismuthate nanoflakes with the monoclinic CaBi₂O₄ phase. The reaction time-dependent results further confirm that the calcium bismuthate nanoflakes originate from the nanoscale particles.

On the basis of the hydrothermal growth condition-dependent experiments, the formation and growth of the calcium bismuthate nanoflakes may be explained by a CTAB-assisted hydrothermal growth process. During the formation process of the calcium bismuthate nanoflakes, CTAB acts as a structure-directing agent which controls the surface free energy promoting the growth of the calcium bismuthate nanoflakes. At the initial hydrothermal reaction stage with low hydrothermal temperature and short reaction time, triclinic Bi₂O₃ is generated from the decomposition of sodium bismuthate. Bismuth oxide and calcium chloride react to form calcium bismuthate. Calcium bismuthate in the hydrothermal solution reaches a super-saturated state and precipitates from the hydrothermal solution forming the nanoscale particles which act as the seeds of the nanoflakes. CTAB molecules are adsorbed to the surface of the calcium bismuthate seeds forming a micro-emulsion cavity system, lowering free energy and inducing the formation of calcium bismuthate nanoflakes [53]. With increasing the reaction temperature, reaction time and CTAB concentration, the calcium bismuthate nanoflakes with the monoclinic CaBi₂O₄ phase are finally formed.

3.3. Solid UV-vis Diffuse Reflectance Spectrum of the Calcium Bismuthate Nanoflakes

Tauc plot of the \((\text{A}hv)^{1/2}\) versus \((hv)\) for the solid UV-vis diffuse reflectance spectrum of the calcium bismuthate nanoflakes is shown in Fig. (10) that analyzes the optical absorption ability and bandgap of the obtained nanoflakes. The inset in the bottom-right part of Fig. (10) shows the solid UV-vis diffuse reflectance spectrum of the calcium bismuthate nanoflakes obtained at 180°C for 24 h using 5wt.% CTAB. The calcium bismuthate nanoflakes have an absorption edge at about 561 nm in the visible light region. The bandgap of the calcium bismuthate nanoflakes is calculated to be 2.21 eV. It is evident that the calcium bismuthate nanoflakes exhibit good visible light absorption ability. Comparing with the bandgap of the calcium bismuthate nanoscale particles (2.47 eV) reported by Shtarev et al. [58], the obtained calcium bismuthate nanoflakes exhibit a smaller bandgap which may possess better photocatalytic performance.
3.4. The Photocatalytic Performance of the Calcium Bismuthate Nanoflakes

The photocatalytic activity of the calcium bismuthate nanoflakes obtained at 180°C for 24 h using 5wt.% CTAB was evaluated under solar light irradiation at the time interval of 1 h. Fig. (11) shows the UV-vis absorption spectra of the GV solution with the concentration of 10 mg·L⁻¹ under solar light irradiation for different time intervals and GV concentration change ratio. The intensity of the absorption peak located at 583 nm decreases obviously by prolonging the irradiation time (Fig. 11a). After the GV solution was irradiated by solar light for 6 h, the color of the GV solution changed from purple to colorless. It can also be observed from Fig. (11b) that the GV degradation efficiency is negligible only in the presence of the calcium bismuthate nanoflakes or solar light irradiation. However, the degradation ratio in the presence of the calcium bismuthate nanoflakes and solar light irradiation is found to be 39.5%, 57.7%, 74.6%, 87.2%, 95.3% and 100% after 1 h, 2 h, 3 h, 4 h, 5 h and 6 h irradiation, respectively. The result shows that the GV degradation contributes to the calcium bismuthate nanoflakes and solar light. The photocatalytic degradation efficiency is shown to increase with an increase in the solar light irradiation time suggesting that the calcium bismuthate nanoflakes have remarkable and persistent photocatalytic performance. The photocatalytic activity of the calcium bismuthate nanoflakes is high enough to completely degrade GV under the solar light irradiation for 6 h. The kinetics of the photocatalytic degradation of the GV can be analyzed by the first-order reaction rate described as the equation \( \ln(\frac{A}{A_0}) = -kt \). Where \( A \) refers to the GV absorbance at the irradiation time \( t \), \( A_0 \) refers to the GV absorbance without solar light irradiation and \( k \) refers to the apparent first-order rate constant (h⁻¹). Fig. (12) shows the kinetic curve of the photocatalytic degradation of GV by the calcium bismuthate nanoflakes. The equation is calculated to be \( \ln(\frac{A}{A_0}) = -0.4425t \). The rate constant is calculated to be 0.4425 h⁻¹ for the calcium bismuthate nanoflakes. The correlation constant is found to be 0.9833.

The role of the dosage of the calcium bismuthate nanoflakes in the degradation efficiency of the GV was investigated from 2.5 to 10 mg/10 mL GV solution with the irradiation time of 6 h and GV concentration of 10 mg·L⁻¹. The UV-vis absorption spectra and GV degradation ratio are shown in Fig. (13). As the dosage of the calcium bismuthate nanoflakes increases from 2.5 to 10 mg/10 mL GV solution, the photocatalytic degradation ratio increases from 53.7% to 100%. The calcium bismuthate nanoflakes have a specific surface area of 39.1 m² g⁻¹. A large amount of activity sites of the calcium bismuthate nanoflakes lead to the improvement in the photocatalytic efficiency for the removal of GV.

The mechanisms of dye degradation in photocatalytic reactions are complex and most of the time contributed by radical chain reactions. A possible photocatalytic mechanism for the degradation of GV over the calcium bismuthate nanoflakes has been analyzed. Under the solar light irradiation, the charge carriers are produced and photo-generated holes...
are transferred to the surface of the calcium bismuthate nanoflakes. The photo-generated electrons are excited from the valence band of the calcium bismuthate nanoflakes to the conduction band when the calcium bismuthate nanoflakes absorb the energy of solar light. The degradation process of the adsorbed GV molecules occurs due to the role of the hydroxyl radicals [79]. GV can be degraded by hydroxyl radicals. The GV degradation results using 10 mg calcium bismuthate nanoflakes irradiating for different times were confirmed with TOC (Fig. 14). The total mineralization ratio for GV increases from 33% to 97% with the irradiation time increasing from 1 h to 6 h.

GV concentration is considered to be an important parameter for the removal of the GV. The role of different initial GV concentration has been analyzed by varying the GV concentration from 2.5 to 20 mg·L⁻¹ with the irradiation time and content of the calcium bismuthate nanoflakes of 6 h and 10 mg/10 mL GV solution, respectively. The relationship between the GV concentration change ratio and GV concentration is shown in Fig. 15. From the curve, it can be found that the GV with a concentration less than 10 mg·L⁻¹ can be totally degraded. The GV degradation ratio decreases rapidly with increasing the initial GV concentration from 10 to 20 mg·L⁻¹. The GV degradation ratio decreases to 39.83%. With increasing the GV concentration, more GV molecules cover the surface of the calcium bismuthate nanoflakes hindering the adsorption of the solar light by the calcium bismuthate nanoflakes and decreasing the active sites of the nanoflakes.

**Fig. (13).** (a) UV-vis absorption spectra of the GV solution treated by the calcium bismuthate nanoflakes with different dosages in 10 mL solution under solar light irradiation. (b) GV concentration change ratio. Irradiation time, 6 h; GV concentration, 10 mg·L⁻¹. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

**Fig. (14).** TOC degradation efficiency for GV treated by the calcium bismuthate nanoflakes in 10 mL GV solution after different irradiation times. Calcium bismuthate nanoflake, 10 mg; GV concentration, 10 mg·L⁻¹. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

**Fig. (15).** GV concentration change ratio using the GV with different initial concentrations. Irradiation time, 6 h; Content of the calcium bismuthate nanoflakes, 10 mg/10 mL GV solution. (A higher resolution / colour version of this figure is available in the electronic copy of the article).
Fig. (16). GV concentration change ratio with the cycle times after the cyclic experiments for the GV degradation using the calcium bismuthate nanoflakes under natural solar light. Irradiation time, 6 h; Nanoflake dosage, 10 mg/mL GV solution; GV concentration, 10 mg·L–1. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

Recyclability and reusability are important for the application of photocatalysts to treat organic pollutants [80, 81]. Therefore, the recyclability and reusability of the calcium bismuthate nanoflakes for the treatment of GV under natural solar light were evaluated by cycle experiments. The calcium bismuthate nanoflakes were collected and washed using distilled water after each cycle experiment. Fig. (16) shows the GV degradation ratio with the cycle time. It is observed that the GV degradation ratio decreases slightly with increasing recycle time. After the calcium bismuthate nanoflakes were used for 6 times, the GV degradation ratio still reached 92.2%. The decrease may be caused by the loss of the calcium bismuthate nanoflakes during the photocatalytic cycle process. The results show that the obtained calcium bismuthate nanoflakes possess good photocatalytic stability. To further demonstrate the stability of the calcium bismuthate nanoflakes after photocatalytic cycles, the transmission electron microscopy and XRD pattern of the calcium bismuthate nanoflakes after six cycles are shown in Fig. (17). It is observed that the morphology of the nanoflakes is similar to that before photocatalytic cycles. The nanoflakes still maintain a single crystalline structure. XRD patterns of the calcium bismuthate nanoflakes before and after photocatalytic experiments are similar. The calcium bismuthate nanoflakes are considered as a stable photocatalyst for the degradation of organic pollutants.

CONCLUSION

In summary, calcium bismuthate nanoflakes have been synthesized by a facile hydrothermal route assisted by CTAB. The calcium bismuthate nanoflakes possess a single crystalline monoclinic CaBi₂O₄ phase with a thickness of about 40 nm. The size of the whole nanoflakes is about 10 μm. The solid UV-vis diffuse reflectance spectrum shows that the bandgap of the nanoflakes is 2.21 eV. The morphology, size and phase of the calcium bismuthate products are closely dependent on the hydrothermal temperature, reaction time and CTAB concentration. CTAB plays an essential role in the formation of the calcium bismuthate nanoflakes. The calcium bismuthate nanoflakes exhibit good photocatalytic activity for the degradation of GV under natural solar light irradiation. The photocatalytic degradation efficiency for GV increases with increasing irradiation time and dosage of the nanoflakes. The GV with a concentration of 10 mg·L⁻¹ and a volume of 10 mL can be totally removed using 10 mg calcium bismuthate nanoflakes under natural solar light irradiation for 6 h.

ETHICS APPROVAL AND CONSENT TO PARTICIPATE

Not applicable.

HUMAN AND ANIMAL RIGHTS

No Animal/Humans were used for studies that are the basis of the research.

Fig. (17). (a) TEM image of the calcium bismuthate nanoflakes after 6 cyclic experiments for the treatment of GV, the inset in the upper-left part is the HRTEM image of the nanoflakes. (b) XRD pattern of the calcium bismuthate nanoflakes before the photocatalytic experiments (a) after 6 cyclic experiments (b). Irradiation time, 6 h; Nanoflake dosage, 10 mg/mL GV solution; GV concentration, 10 mg·L⁻¹. (A higher resolution / colour version of this figure is available in the electronic copy of the article).
CONSENT FOR PUBLICATION
Not applicable.

AVAILABILITY OF DATA AND MATERIALS
Not applicable.

FUNDING
This work was supported by the Natural Science Foundation of Anhui Province of P.R. China (2008085ME172), Natural Science Foundation of Fujian Province of P.R. China (2019J01872) and Student Innovation and Entrepreneurship Training Program of P.R. China (Grant No. 201910360014, 201910360018).

CONFLICT OF INTEREST
The authors declare no conflict of interest, financial or otherwise.

ACKNOWLEDGEMENTS
Declared none.

REFERENCES
[24] Aparecida, K.; Gusmão, G.; Gurgel, L.V.A.; Melo, T.M.S.; Gil, L.F. Application of succinylated sugarcane bagasse as adsorbent to...


