High photocatalytic activity of oxychloride CaBiO$_2$Cl under visible light irradiation

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Oxychloride CaBiO$_2$Cl was shown as a highly active photocatalyst which can efficiently decompose methylene blue (MB), and yield high photocurrent density under ultraviolet (UV) light or visible-light irradiation. Density functional calculations revealed that the valence band (VB) was not only composed of the O 2p hybridized orbital, but also a little the Cl 3p and Bi 6p orbitals. During the calcination synthesis process, a certain amount of oxygen vacancies existed in the prepared samples, which resulted in the formation of surface hydroxyl groups. The photocatalytic activities for MB degradation were strongly dependent on the surface hydroxyl groups. By evaluation of the infrared transmission spectra (FTIR) of the series of samples, a correlation between the number of surface hydroxyl groups and the photocatalytic activity was revealed. The surface hydroxyl groups were important active sites for producing active hydroxyl radicals and a dominant factor in controlling the performance of the samples.

1. Introduction

Over the last 30 years, the studies of semiconductor photocatalysts for clean hydrogen energy production and environment decontamination have attracted much interest. From the viewpoint of solar energy utilization, the development of a photocatalyst with a high activity under visible-light is indispensable. One effective way to narrow the band gap is to elevate the valence band of photocatalysts into a more negative position by anion substitution. The doping of foreign elements into UV active metal oxides is a conventional method employed for the preparation of visible-light-responsive photocatalysts. However, dopants in the photocatalyst act not only as visible-light absorption centers, but also as recombination sites between photogenerated electrons and holes. In contrast, some non-oxides, for example (oxy)nitrides and oxsulfides, contain N or S as constituent elements that form the top of the valence band. Note that this type of material differs from materials doped with nitrogen or sulfur. Thus, photogenerated holes can migrate smoothly in the valence band of the material. A range of non-oxide materials for photocatalytic overall water splitting have been developed by Domen’s group. They found that non-oxides could function as stable photocatalysts for water reduction and oxidation under visible-light irradiation.

The discovery of non-oxide photocatalysts is expected to reinvigorate research on photocatalysts for solar energy. Recently, Bi-based oxychlorides have drawn attention for their potential application as novel photocatalysts owing to their unique layered structure and high chemical stabilities. This layered structure is believed to enable the effective separation of the photo-induced electron-hole pairs, assisting a high photocatalytic performance. As a new family of layered bismuth compounds, their potential fields of application are worthy of further research. CaBiO$_2$Cl, known as a typical Bi-based oxychloride, is derived from the ideal Sillen X1 structure type, which is composed of fluorite-like [CaBiO$_2$]$^+$ layers separated by single Cl$^-$ layers as shown in Fig. 1. In general, CaBiO$_2$Cl has garnered significant attention related to its crystal structure and photoluminescence properties. Although the photocatalytic activity of CaBiO$_2$Cl was reported recently, hardly any attention has been paid to analysis of its photophysical properties and photocatalytic mechanism. In this work, the photocatalytic performances of CaBiO$_2$Cl were investigated systematically. The photochemical properties of CaBiO$_2$Cl were demonstrated by the photocatalytic decomposition of MB and photocurrent measurements under UV and visible-light irradiation. A possible photocatalytic pathway was also suggested on the basis of the understanding of the photocatalytic properties of CaBiO$_2$Cl.

2. Experimental section

2.1 Synthesis of samples

CaBiO$_2$Cl samples were prepared by a two-step process. All chemicals used were analytic grade reagents without further purification. The starting materials of Bi(NO$_3$)$_3$ and KCl (1 : 1
The measurements of the amount of hydroxyl radical generated were conducted according to the literature.\textsuperscript{23} 100 mg of photocatalyst was suspended in 80 mL aqueous solution containing 10 mM NaOH and 3 mM terephthalic acid (TA). Before exposure to UV light irradiation, the suspension was stirred in the dark for 30 min. Then, 5 mL of the solution was taken out every 20 min and centrifuged for fluorescence spectrum measurements. The employed excitation light in recording fluorescence spectra was 320 nm. The photocatalytic activities of the CaBiO\textsubscript{2}Cl samples were evaluated by the degradation of MB under an 11 W bactericidal lamp at 254 nm and a 500 W Xe lamp with a 400 nm cutoff filter. The average light intensities were 0.8 mW cm\textsuperscript{-2} and 28 mW cm\textsuperscript{-2}, respectively, for the bactericidal lamp and Xe lamp. The reaction cell was placed in a sealed black box of which the top was opened and the cutoff filters were placed to provide visible-light irradiation. A picture of the photocatalytic instruments used for UV light and visible-light irradiation is shown in Fig. S2. In each run, 50 mg of the CaBiO\textsubscript{2}Cl catalyst was added to 100 mL of the MB solution. After the suspension was stirred for 40 min, the light was turned on to initiate the reaction. The concentration of the MB solution was monitored using a Hitachi UV-vis spectrophotometer. The electrochemical and photoelectrochemical studies were performed on a CHI 660B electrochemical system (Shanghai, China) using a standard three-electrode cell with a working electrode, a platinum wire counter electrode, and a standard calomel electrode (SCE) reference. The working electrodes were prepared by dip-coating: briefly, 20 mg of photocatalyst was suspended in 1 mL ethanol to produce slurry, which was then dip-coated on a 20 mm \times 30 mm indium–tin oxide (ITO) glass electrode. Electrodes were exposed to air for 1 day to eliminate ethanol and subsequently dried at 353 K for 1 day. All investigated working electrodes were of similar thickness. Photoelectrochemical properties were measured with a 500 W Xe lamp and a 18 W bactericidal lamp. Unless otherwise stated, the average light intensities were 45 mW cm\textsuperscript{-2} and 1.64 mW cm\textsuperscript{-2}, respectively, for the Xe lamp with a 400 nm cutoff filter and the bactericidal lamp. During all measurements, the electrolyte was 0.1 M Na\textsubscript{2}SO\textsubscript{4} solution.

2.4 Calculation method of band structure

The quantum-mechanical calculations performed here were based on density functional theory (DFT). Exchange-correlation effects were taken into account by using the generalized gradient approximation (GGA).\textsuperscript{24,25} The total energy code CASTEP was used, which utilized pseudopotentials to describe electron-ion interactions and represents electronic wave functions using a plane-wave basis set. The kinetic energy cutoff was set at 340 eV.

3. Results and discussion

3.1 Structure and properties

Fig. 2 shows the XRD patterns for the samples calcinated at different temperatures for 12 h. The calcination temperatures had an important role during the formation of CaBiO\textsubscript{2}Cl samples. After the solid-state reaction at 600 °C for 12 h, the intensity of the peaks, which was attributed to BiOCl and Ca(NO\textsubscript{3})\textsubscript{2}, disappeared, some new peaks formed, and a coexistent phase (CaBiO\textsubscript{2}Cl and the other oxides) appeared and strengthened. As the temperature was raised to 700 °C,
CaBiO$_2$Cl with a monoclinic structure was formed completely. This indicated that the optimal temperature for the formation of CaBiO$_2$Cl by this method was above 700 °C. Prolonging the reaction time (from 12 to 24 h) did not significantly improve the crystallinity. When the reaction temperature was increased to 800 or 1000 °C, the XRD peaks became much sharper and more intense (moreover, the estimates of crystal size were shown in Table 1). After refinement, the cell constants of CaBiO$_2$Cl were calculated to be $a = 7.733$ Å, $b = 4.126$ Å, $c = 6.396$ Å, $\beta = 105.235^\circ$, which are consistent with the literature data.$^{19}$

DRS spectra of the as-prepared samples were shown in Fig. 3. The CaBiO$_2$Cl samples presented photoabsorption ability from the UV light to the visible-light region. It was noteworthy that the adsorption onsets of the samples were dependent strongly on the calcination temperature. When the temperatures were 700 and 800 °C, the samples showed the same absorption onset. The band gaps of the samples were estimated to be 2.73 eV. However, the absorption onsets of the samples had a long tail, which was almost similar to that of the TiO$_2$ doped with nitrogen, when the temperature was increased to 900 °C and 1000 °C. Generally, for higher temperatures, it is easier for oxygen vacancies to form in the structure and the optical absorption property is greatly influenced by oxygen vacancies. The color of the samples (temperature = 700 and 800 °C) was pale-yellow, whereas the samples were yellowish in color when the temperature = 900 and 1000 °C, as predicted from their photoabsorption spectra.

According to the literature, trivalent bismuth cations in inorganic compounds commonly exhibit interesting luminescence properties originating from the excitation and relaxation of their 6$s^2$ inert lone pair electrons.$^{26-28}$ In our system, CaBiO$_2$Cl exhibited Bi 6s6p$\rightarrow$6$s^2$ emission under UV irradiation. Excitation and emission spectra of the as-prepared samples were presented in Fig. 4. The fluorescence signal of the CaBiO$_2$Cl calcinated at 700 °C exhibited emission peak maxima at about 410 nm. However, with the increase of calcination temperature adopted in the synthesis of CaBiO$_2$Cl, the emission peaks maxima were blue-shifted approximately 10 nm for the samples calcinated at 700–800 °C. The blue-shifts of the emission peak maxima can be due to the slight change of crystal environment around Bi$^{3+}$. Many studies have reported that luminescence is closely related to structural defects, such as oxygen vacancies.$^{29,30}$ Hence, in our work, higher calcination temperature leads to formation of oxygen vacancies, which influences the crystal environment of CaBiO$_2$Cl.

The O 1s XPS result of CaBiO$_2$Cl calcinated at 700 °C and 900 °C was shown in Fig. 5. The binding energy of O 1s was 531.4 eV, with a big shoulder at 530.0 eV. The binding energy at 531.4 eV could be ascribed to the characteristic O species in the oxide form, while 530.0 eV might be characteristic of O species in surface hydroxyl groups absorbed on CaBiO$_2$Cl.$^{31}$ In the case of CaBiO$_2$Cl calcinated at 900 °C, the peak of the binding energy at 530.0 eV intensified, which was attributable to the increase of surface hydroxyl content on the sample surface. Because of the oxygen vacancies easily formed in the surface of CaBiO$_2$Cl calcinated at higher temperature, it is much more defected than the surface of CaBiO$_2$Cl calcinated at lower temperature; as a consequence, more surface hydroxyl groups might form.

### Table 1 BET surface areas and crystal sizes of the temperature series samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>600 °C</th>
<th>700 °C</th>
<th>800 °C</th>
<th>900 °C</th>
<th>1000 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface areas (m$^2$ g$^{-1}$)</td>
<td>1.41</td>
<td>1.31</td>
<td>1.26</td>
<td>1.17</td>
<td>0.93</td>
</tr>
<tr>
<td>Crystal size (nm)</td>
<td>90</td>
<td>120</td>
<td>145</td>
<td>174</td>
<td>213</td>
</tr>
</tbody>
</table>

$^a$ Crystal size of the samples calculated by the Scherrer equation: $D_c = K\lambda/(\beta\cos\theta)$ using the parameters of the (001) peak.

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Fig. 2 XRD patterns of the samples calcinated at different temperatures.

Fig. 3 UV-vis spectra of the samples calcinated at different temperatures.

Fig. 4 Room temperature excitation and emission spectra of CaBiO$_2$Cl calcinated at different temperatures.
3.2 Band structure

The photocatalytic activity of a semiconductor is related to its band structure. The calculated electronic band structure of CaBiO₂Cl is shown in Fig. 6A. The Fermi energy, defined as the highest occupied energy level, has been taken as the valence band maximum (VBM). The VBM is located at the B point. And the conduction band minimum (CBM) is situated in the region of the D–E points. This means that CaBiO₂Cl is an indirect semiconductor, in good agreement with the previous result.²⁰ The minimum band gap between VBM and CBM is about 2.7 eV, slightly smaller than the actual value obtained by the optical absorption spectrum, which is due to the fact that this method has an error for band gap calculation.³²

Fig. 6B shows the total density of states (TDOS) and main partial density of states (PDOS), corresponding to the energy region in Fig. 6A. The highest occupied band corresponding to VB was not only found to be composed of the O 2p orbital, but also a little of the Cl 3p and Bi 6p orbitals. This result is obviously different from foreign elements creating impurity levels in the forbidden band in doped oxides. A large dispersion was observed in the hybridized orbitals in the VB of CaBiO₂Cl, suggesting that the photoexcited charges have a high mobility in the VB.³³ This may lead to suppression of the recombination of electron-hole pairs and a relatively higher photochemical activity of the material than that of doped oxides. We also found that the bottom of the CB was mainly composed of the hybridized Bi 6p and Ca 3d orbitals. The contribution of O 2p to the CB seemed to be much smaller than that in the oxides whose conduction electron was O 2p.

3.3 Photocatalytic performances

On the basis of the surface characterization results described above, it is now instructive to compare the photocatalytic activity of all samples. Fig. 7A shows the degradation curves for MB under UV irradiation in the presence of CaBiO₂Cl calcinated at different temperatures. The blank test and photolysis of MB confirmed that MB was slightly degraded in the dark and under UV light without photocatalysts, indicating that the adsorption action and photolysis of MB can be ignored. The calcination temperature has a significant effect on the degradation rate. As shown in the Fig. 7A, the sample prepared at 600 °C exhibited the lowest photocatalytic activity (58% of MB was degraded in 2 h). That sample was a mixed phase and not of high crystallinity, which was confirmed by the XRD result. A lot of defects could act as an electron-hole recombination center. So the photocatalytic activity was low. Before 900 °C, the higher the treatment temperature was, the higher the activities were. When the temperature further increased to 1000 °C, the activity decreased. The degradation degrees of MB were 61.9, 77.5, 89.3, and 82.4%, respectively, for the temperatures from 700 to 1000 °C.

Based on the DRS spectra, the series of CaBiO₂Cl samples presented photoabsorption ability from the UV light to the visible-light region. In order to confirm the visible-light-induced photocatalysis, the MB degradation was carried out under visible-light irradiation. For comparison, the MB photodegradation by TiO₂-xNₓ was also performed. It was obvious that MB could be degraded over all the samples under visible-light irradiation (λ > 400 nm) (Fig. 7B). Moreover, most samples exhibited higher photoactivities than our prepared TiO₂-xNₓ. Similar to UV light induced degradation, the photocatalytic activity of the samples for the decomposition of MB under visible-light irradiation also depended on the calcination temperature, and the best performance was also realized on
900 °C. More than 74% of the MB was decomposed in 4 h. From these results, it was obvious that CaBiO₂Cl is a visible-light sensitive oxychloride.

The XRD pattern of a sample after five runs is shown in Fig. S3. The XRD peaks became broader and weak, indicating that CaBiO₂Cl is not very stable in this system where photocorrosion might occur during the photocatalytic process. In general, non-oxides are unstable because the non-oxygen anions are sensitive to oxidation by photogenerated holes, for example CdS. In order to improve its stability, experiments on the mechanism of photocatalytic activity are underway.

3.4 Photoelectrochemical properties

The mobilities of the electrons generated in the photocatalyst can be directly monitored by the photocurrent, and the rate should directly correlate with the photocatalytic activity of the material. Fig. 8A shows the photocurrent of samples generated in electrolyte under UV light. The potential of the working electrode against a Pt counter electrode was set at 0.0 V. Without light irradiation, the photocurrent was nearly zero. With light irradiation, a negative photocurrent was observed. CaBiO₂Cl calcinated at 900 °C generated the highest photocurrent among all samples, while the photocurrent of the 600 °C sample was the lowest, which was about one-fourth of the 900 °C sample. It can also be found that the order of photocurrent values for the samples was consistent with the order of their photocatalytic activities, showing the photocurrent was positively relevant to the photocatalytic activity. The generation of photoelectrons was the critical initial step of the photocatalytic reaction, and the rate directly governed the photocatalytic activity. We further investigated the photocurrent of samples under visible-light irradiation (λ > 400 nm) (Fig. 8B). It also can be seen that the sample obtained at 900 °C generated the highest photocurrent. Comparing with UV light irradiation, the photocurrent of most samples under visible-light seemed to be increased. The increase in the photocurrent was attributed to the different power of the lamps (as shown in Experimental section 2.3), leading to a different number of photogenerated electrons. The photocurrent conversion in UV and visible-light further confirmed that CaBiO₂Cl was a potential photofunctional material.

3.5 Mechanism of photocatalytic activity

The photocatalytic activity for decomposing MB and the photoelectrochemical properties of CaBiO₂Cl were found to be
dependent on the calcination temperature. The activity increased with increasing calcination temperature up to 900 °C. However, the activity for the sample prepared at 1000 °C dropped obviously. Note that thermal annealing of CaBiO₂Cl at temperatures above 900 °C largely caused a loss of surface area of the sample (Table 1); as a result, the sample calcinated at 1000 °C had lower photocatalytic activity. In the range of 700–900 °C, although calcination induced a small increase in crystal size and a slight decrease in surface area, the sample still exhibited enhanced activity with increasing temperature. This indicated that other factors might favorably influence the photocatalytic performance of CaBiO₂Cl.

Surface hydroxyl groups are known to play an important role in photocatalysis; they react with photogenerated holes, producing active hydroxyl radicals. In addition, surface hydroxyl groups can act as surface sites for adsorbing organic molecules, which also efficiently capture photogenerated holes. The trapping of holes stabilizes photogenerated electron-hole pairs, improving photocatalytic efficiency. Hence, surface hydroxyl groups are considered as the main factor influencing the photocatalytic activity. The FTIR spectra of the samples in the region of 4000–1000 cm⁻¹, where O–H stretching modes were expected, were shown in Fig. 9. CaBiO₂Cl samples showed bands at 1400–1500 cm⁻¹, which could be attributed to Ca–Bi–O stretching modes. The peaks of 1630 cm⁻¹ and the broad band at 3300–3600 cm⁻¹ were assigned to the bending and stretching vibration of O–H. The intensities of O–H vibration bands increased with calcination temperature, indicating the number of surface hydroxyl groups was increasing. The O–H vibration is sensitive to a change of the environment around the ion; therefore, O–H absorption spectra can be used as a probe for defects. According to the DRS and luminescence spectra (Fig. 3 and 4), it can be speculated that oxygen vacancies could exist in the samples. Moreover, the content of oxygen vacancies increased with the increase in calcination temperature. As a consequence, as we know, more cations with unsaturated coordination exist in the surface, and more surface hydroxyl groups might form.

The photocatalytic tests were carried out on CaBiO₂Cl materials suspended in an aqueous medium. The surface hydroxyl groups observed in the FTIR spectra should be considered as a precursor for the actual site during the reaction. It is believed that this site has the highest efficiency in trapping the photo-generated holes to form hydroxyl radicals. It is known that hydroxyl radicals can react with terephthalic acid (TA) to generate 2-hydroxy terephthalic acid (TAOH), which emits a unique fluorescence at 426 nm. As shown in Fig. 10A, obvious fluorescence signals associated with TAOH were generated upon irradiation of the CaBiO₂Cl calcinated at 900 °C suspended in 3 mM TA solution for different irradiation times. The nearly linear relationship between fluorescence intensity and irradiation time confirmed CaBiO₂Cl as a photocatalyst, and more importantly, the synthesized CaBiO₂Cl could generate the photocatalytic hydroxyl radicals. Time dependencies of the fluorescence intensity with CaBiO₂Cl calcinated at different temperatures were also displayed in Fig. 10B. It can be seen that a variation in calcination temperature greatly influenced the generation of hydroxyl radicals and the generation rate increased from 700 to 1000 °C. Consequently, on the basis of the FTIR results, CaBiO₂Cl samples calcinated at higher temperatures had a higher density of surface hydroxyl groups for capturing photogenerated holes, thereby generating more hydroxyl radical population. Thus, the activities of samples were enhanced from 700 to 900 °C. The decreased activity of CaBiO₂Cl calcinated at 1000 °C is assumed to result from a loss of surface area due to thermal annealing. Therefore, the optimum calcination temperature for CaBiO₂Cl is 900 °C, and the surface hydroxyl groups are the main factor influencing the photocatalytic activity.

![Fig. 9](image1.jpg)

**Fig. 9** FTIR spectra of the samples calcinated at different temperatures.

![Fig. 10](image2.jpg)

**Fig. 10** Fluorescence spectra of the UV light irradiated CaBiO₂Cl calcinated at 900 °C in suspension in 3 mM terephthalic acid at different irradiation times (A). Time dependence of the fluorescence intensity at 426 nm with CaBiO₂Cl calcinated at different temperatures (B).
1000 °C was attributed to a decrease of surface area and an increase of crystal size (as shown in Table 1). When the temperature of the calcination treatment was too high, too small surface area suppresses the photocatalytic activity.

For photooxidations occurring in aqueous media, the mechanism may involve direct reaction of the organic dye with surface \( h^+_{sb} \), indirect reaction with hydroxyl radicals, or a dual mechanism involving both surface \( h^+_{sb} \) and hydroxyl radicals (reaction 1).

\[
\text{surface } h^+_{sb} + \text{hydroxyl radicals + dye (MB)} \rightarrow \text{products (1)}
\]

To study the process of the photooxidation of CaBiO\(_2\)Cl, experiments were carried out by adding tert-butyl alcohol to minimize the formation of hydroxyl radicals. The results were shown in Fig. 11. It was interesting to see that the addition of tert-butyl alcohol reduced the photodegradation rate of MB over the CaBiO\(_2\)Cl samples. However, parts of the photocatalytic activity still remained. This implied that the MB degradation on CaBiO\(_2\)Cl seemed to be initiated by a dual mechanism involving both surface \( h^+_{sb} \) and hydroxyl radicals. The different mechanisms of photodegradation among the samples were attributed to the different number of hydroxyl radicals.

### 4. Conclusion

CaBiO\(_2\)Cl was found as an effective photocatalyst for MB degradation under UV and visible-light irradiation. Moreover, the photocurrent conversion in the UV and visible-light further confirmed that CaBiO\(_2\)Cl was a potential photofunctional material. The photocatalytic activity of the CaBiO\(_2\)Cl samples was mainly governed by the number of surface hydroxyl groups which was induced by oxygen vacancies formed during calcination processes. High photocatalytic performances of the samples can be obtained by increasing the number of surface hydroxyl groups \textit{via} control of the reaction conditions.

### Acknowledgements

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### References


Fig. 11  Effect of tert-butyl alcohol addition on the MB degradation over CaBiO\(_2\)Cl calcinated at different temperatures. [tert-butyl alcohol] = 1 mM.