

Synthesis and Photocatalytic Activity of M-doped CaBiO₂Cl (M = Ag, Co, and Ni) under Visible Light

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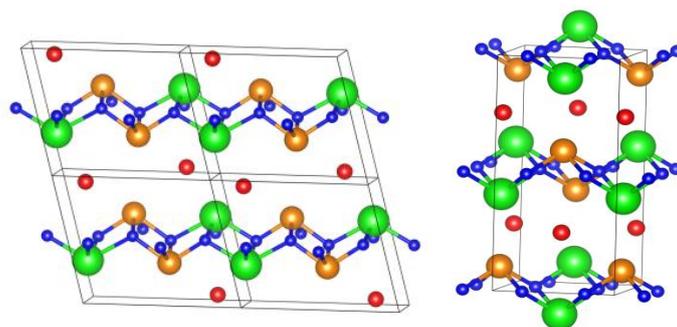
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Abstract. CaBiO₂Cl-based photocatalysts doped with M (M = Ag, Co, and Ni) were synthesized by solid state reaction method. The microstructure and morphology of catalysts were characterized by using X-ray diffraction analysis (XRD), field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDXS) and UV-vis diffuse reflectance spectra techniques. The photocatalytic activities of pure CaBiO₂Cl and M-CaBiO₂Cl catalysts were further evaluated by degrading methylene blue (MB) under visible-light irradiation. The results suggested that in comparison with pure CaBiO₂Cl, the photocatalytic activity of M-CaBiO₂Cl composite photocatalysts is greatly improved. The possible mechanism of enhancing the catalytic activity of M-CaBiO₂Cl composite photocatalysts was further discussed.

Introduction

Semiconductor photocatalysts for clean hydrogen energy production and environment decontamination have attracted much interest since the photocatalytic activity of TiO₂ was first reported by Fujishima and Honda in 1972. Currently, TiO₂-based semiconductors have been considered as one of the efficient and active photocatalysts in practical application due to the intrinsic advantages such as outstanding oxidative power, high stability, and low cost [1-6]. However, TiO₂ with larger band gap (about 3.2 eV for anatase TiO₂) has no visible-light response. In addition, high recombination rate of photogenerated electron-hole pairs in TiO₂ leading to a relatively low quantum yield also hinders its application. It is essential to exploit new visible-light responsive photocatalysts with better photocatalytic performance [7-10]. Recently, many bismuth-based compounds such as BiVO₄ [11], Bi₂WO₆ [12], BiOCl [13], CaBi₂O₄ [14], Bi₂O₂CO₃ [15] and Bi₁₂TaO₂₀ [16] have been reported as new photocatalytic materials. Moreover, metal doping modification is also considered as an effective way to improve the photocatalytic properties, since metal additives can not only regulate the widths of band gap of semiconductor photocatalysts efficiently to optimize the band structure, but also improve the morphology of photocatalysts obviously [17-18].

CaBiO₂Cl is a typical Bi-based oxychloride and belongs to the ideal Sillen X1 structure, in which the fluorite-like [CaBiO₂]⁺ layers are separated by the Cl⁻ layers as shown in Fig. 1. Recently, CaBiO₂Cl has been reported as an active photocatalyst for environmental decontamination under visible-light irradiation and shows exciting photocatalytic activity [19-20]. In this study, the CaBiO₂Cl and M-CaBiO₂Cl powders were synthesized successfully via a two-step process. The photochemical properties of M-CaBiO₂Cl were evaluated by the photocatalytic decomposition of MB under visible-light irradiation. The corresponding visible-light photocatalytic activities of pure CaBiO₂Cl and M-CaBiO₂Cl composite catalysts were further discussed in detail.



The green, orange, blue, and red spheres are for Ca, Bi, O, and Cl atoms, respectively

Fig.1 Crystal structure of CaBiO₂Cl

Experimental Methods

Synthesis

All chemicals used in the present experiments were obtained from the commercial sources as analytical reagents. In this paper, the CaBiO₂Cl and M-CaBiO₂Cl powders were synthesized by a two-step process. Firstly, 0.01mol KCl was dissolved in 50ml deionized water and stirred for 15 min at room temperature to get solution A. While 0.01mol Bi(NO₃)₃·5H₂O was dissolved in 5ml HNO₃ of 2 mol/L and stirred for 15min at room temperature to get solution B. White precipitate was obtained immediately after pouring solution A into solution B and the pH value was adjusted to 3 by ammonia and stirring continuously at room temperature for 8h. The precipitate was collected and washed with deionized water and absolute ethanol thoroughly and further dried at 60°C for 12 h in an oven. Secondly, BiOCl and CaCO₃ (1:1 molar ratio) were used to synthesize CaBiO₂Cl by a solid-state reaction. The reactant powders were mixed completely and ground using a mortar and pestle to create a homogeneous mixture. Furthermore, the precursor was obtained by rejoining a certain amount of Co(NO₃)₂, AgNO₃ and Ni(NO₃)₂ into the mixture and stirring for 30 min continuously. Then the precursor was transferred into an alumina crucible and heated in air at 900°C for 12 h in a chamber furnace. Finally, M-CaBiO₂Cl polycrystalline powders were obtained from these reactions.

Characterization

The crystallinity and purity of the as-prepared sample was characterized by using X-ray diffractometer (XRD) (Bruker D8-2-Advanced XRD, Germany) with Cu K α radiation ($\lambda = 0.1541$ nm) from 10°-80°, with a scan speed of 5° min⁻¹. Field emission scanning electron microscopy (FESEM) (Quanta 450 FEG, USA) was used to characterize the surface morphology and texture. The composition of the samples was examined using energy dispersive X-ray spectroscopy (EDXS) (Thermo Noran VANTAG-ESI, USA). The UV-vis absorption spectra of the photocatalysts were obtained by a UV-vis spectrometer (Puxi TU-1901, China) in the range of 200-700 nm. UV-vis diffuse reflectance spectra (UV-vis DRS) of the catalysts were determined with a Puxi TU-1901 spectrophotometer using BaSO₄ as a reference.

Photocatalytic Degradation

The photocatalytic activities of CaBiO₂Cl and M-CaBiO₂Cl photocatalysts were evaluated through degrading methylene blue (MB) under visible light irradiation at room temperature. The 0.10 g powder of photocatalyst was immersed in a quartz beaker containing 100 mL MB solution with a concentration of 5 mg/L. In order to ensure the equilibrium of adsorption/desorption between MB and the photocatalysts, the suspension was stirred in the dark for 30 min. Then the photocatalytic degradation experiment was started by irradiating with a 300 W Xeon arc lamp with a UV cut off to ensure all the incoming wavelengths longer than 420 nm to provide visible-light irradiation ($\lambda > 420$ nm). Moreover, 6 mL of suspensions was taken out using centrifuge tubes in an interval of 20 min. At last, a centrifuge was used to remove the power and the supernatant was

taken for analysis. The absorbance of centrifugal solution was determined at 664 nm by UV-vis spectrophotometer.

Results and Discussion

Fig. 2 shows the XRD patterns of the as-synthesized pure CaBiO_2Cl and M- CaBiO_2Cl powders. It was found that the monoclinic structure phase (JCPDS No. 89-5350) can be indexed in the M- CaBiO_2Cl . The XRD patterns show sharp and strong peaks, indicating the high degree of crystallinity. Furthermore, no other peaks can be observed, meaning high purity of the final products. The results show that metal dopings do not change the parent phase structure of CaBiO_2Cl during the crystallization process and the three metal ions can be doped into CaBiO_2Cl in a solid solution. As shown in Fig. 2, the obvious characteristics of the diffraction peaks shift to higher angle at about 25.96° and 26.96° can be observed. This indicated that three metal ions might enter into the lattice structure of CaBiO_2Cl to replace Bi^{3+} ion and lead to the lattice distortion to some extent [21].

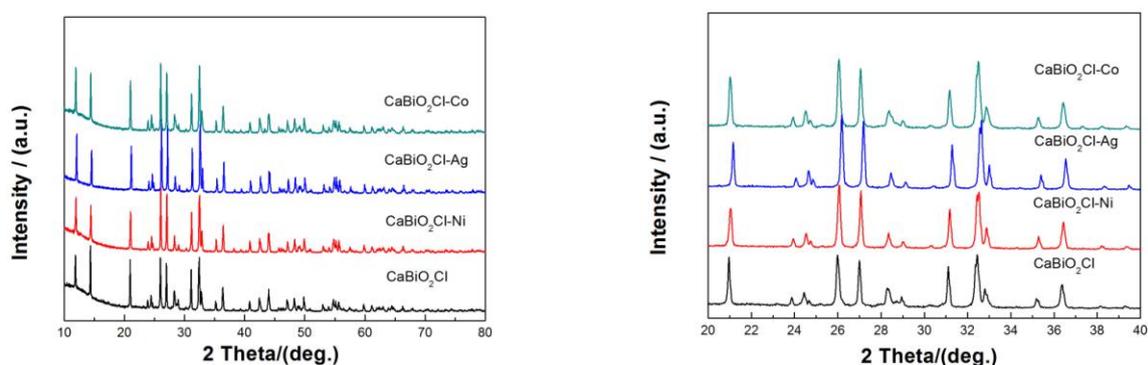


Fig.2 XRD patterns of the pure CaBiO_2Cl and M- CaBiO_2Cl particles

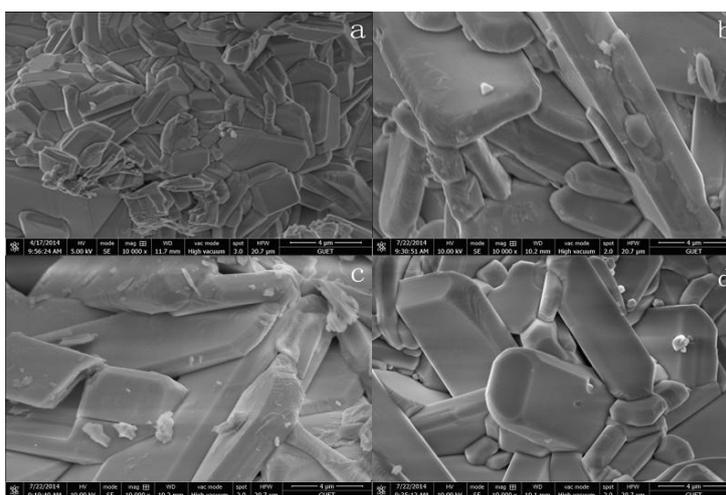


Fig.3 SEM images of pure CaBiO_2Cl and M- CaBiO_2Cl composites: (a) CaBiO_2Cl , (b) Co- CaBiO_2Cl , (c) Ag- CaBiO_2Cl , (d) Ni- CaBiO_2Cl

Fig. 3 shows the morphology and microstructure of the obtained pure CaBiO_2Cl and M- CaBiO_2Cl catalysts measured by the field emission scanning electron microscopy (FESEM). Basically, it can be seen that the products have a brick-like morphology for the pure CaBiO_2Cl and M- CaBiO_2Cl . As can be seen in Fig. 3(a), the average length, width, and height of the brick-like particles are about $3\ \mu\text{m}$, $2\ \mu\text{m}$, and $1\ \mu\text{m}$ for the pure CaBiO_2Cl . For M- CaBiO_2Cl shown in Fig.

3(b), (c), and (d), the average size of particles are obviously larger than the pure CaBiO_2Cl and the corresponding length, width, and height are around $8\ \mu\text{m}$, $4\ \mu\text{m}$, $2\ \mu\text{m}$, respectively. As can be seen in Fig. 2(c) - (d), M- CaBiO_2Cl samples showed better crystallinity and closer arrangement in comparison with pure CaBiO_2Cl . The higher crystallinity would facilitate yielding the higher photocatalytic activity, since the recombination of photogenerated electron-hole pairs can be suppressed in the highly crystalline photocatalysts [22]. As presented in Fig. 4(a)-(c), the elemental composition of the metallic dopants was measured by EDXS. Smaller Co, Ag, and Ni peaks in the spectra can be observed, which indicates the metallic dopants have been substituted into the CaBiO_2Cl structure. This also agrees with the foregoing XRD results.

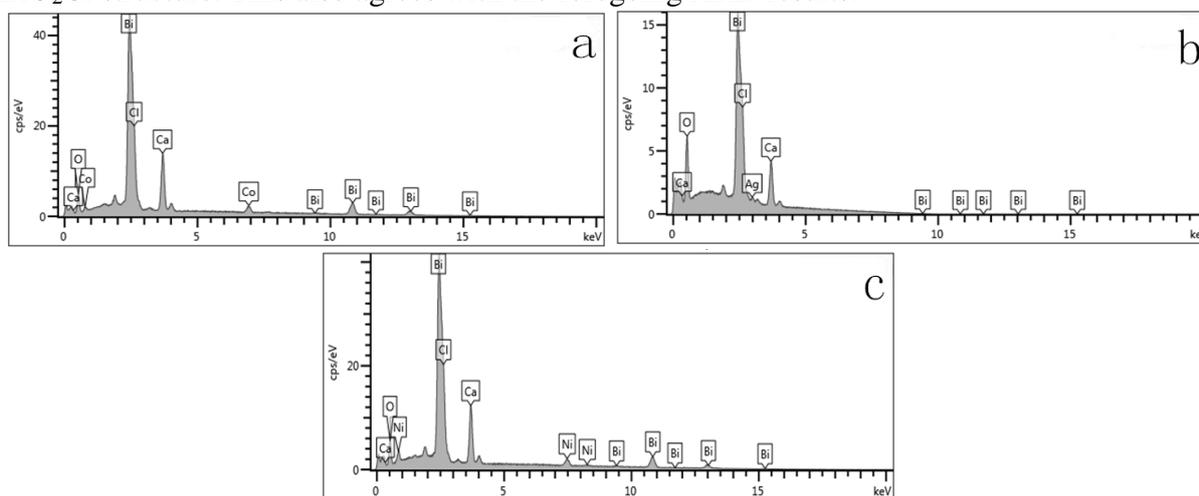


Fig.4 EDXS spectra of (a) Co- CaBiO_2Cl , (b) Ag- CaBiO_2Cl and (c) Ni- CaBiO_2Cl

Fig.4 shows the absorbance as a function of wavelength for pure and M- CaBiO_2Cl . It is clearly visible from the spectra that the absorption edge of M- CaBiO_2Cl is further shifted to the visible region comparing to the pure CaBiO_2Cl sample. The results indicate that the considerable absorption band in the visible light region would enable the utilization of sunlight for the photodegradation of the pollutants. The optical band gap of the pure CaBiO_2Cl sample is estimated to be about 2.64 eV by the extrapolation method, which is similar to values reported in the previous literature [20]. However, The band gap of the catalysts doped with Co, Ag, and Ni are 2.41, 2.50, and 2.34 eV, respectively. This means that the visible-light responsive region of M- CaBiO_2Cl (M = Co, Ag, Ni) composites would be widened in comparison with that of pure CaBiO_2Cl .

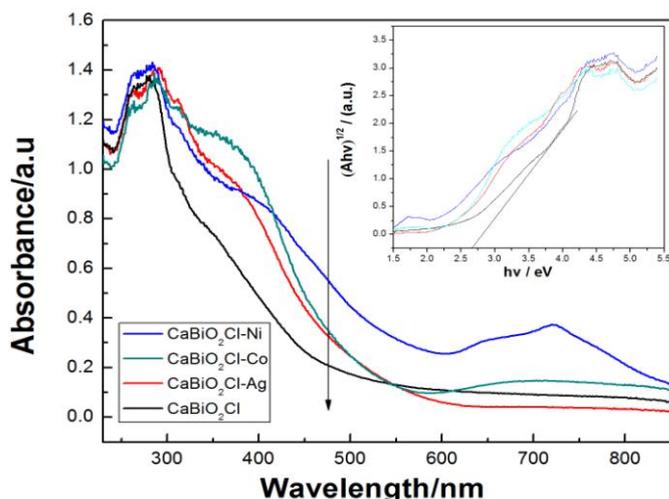


Fig.5 UV-vis diffuse absorption spectra of M- CaBiO_2Cl

The photocatalytic activity of the pure CaBiO_2Cl and $\text{M-CaBiO}_2\text{Cl}$ were evaluated by the degradation of MB (5 mg/L) under both UV and visible-light irradiation with cut off filter to ensure the wavelengths longer than 420 nm. The concentration rate C/C_0 of MB solution as a function of reaction time t under the irradiation of UV-visible light is shown in Fig. 6. As a comparison, MB degradations without any photocatalyst and over pure CaBiO_2Cl were also performed under the same conditions and are shown in Fig. 6. The results show that MB solution cannot be degraded without any photocatalyst, meaning MB solution is little self-degradation and relatively stable under visible light irradiation. For the pure CaBiO_2Cl , the total degradation rate of MB is about 50.9% after 140 min of reaction. While the total degradation rates of MB for $\text{M-CaBiO}_2\text{Cl}$ catalyst are higher than 85% in the same time. It is obvious that Ni-modified CaBiO_2Cl has the highest degradation rates about 95.3% after 140 min. Compared with pure CaBiO_2Cl , the improvement in the photocatalytic activity of $\text{M-CaBiO}_2\text{Cl}$ could be linked to the better morphology in metal modified photocatalyst as presented in the foregoing SEM analysis. $\text{M-CaBiO}_2\text{Cl}$ with higher crystallinity provided the more activity sites. Moreover, the recombination of electron-hole pairs can be suppressed by the doped Ag, Co or Ni ions, since the metal ions additive acting as trap sites can capture photogenerated electrons when the photogenerated electrons were excited under visible-light irradiation.

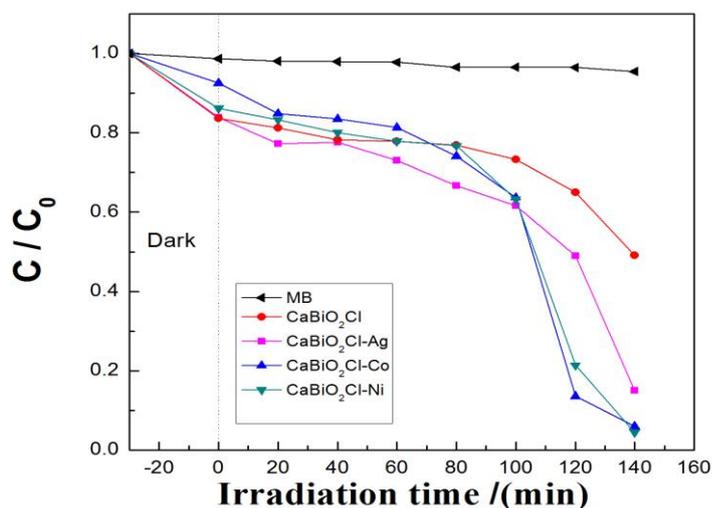


Fig.6 Visible-light induced photocatalytic degradation of MB

Summary

In conclusion, using $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, KCl and CaCO_3 as raw materials and $\text{Co}(\text{NO}_3)_2$, AgNO_3 , $\text{Ni}(\text{NO}_3)_2$ as additive source. $\text{M-doped CaBiO}_2\text{Cl}$ ($\text{M} = \text{Ag}, \text{Co}, \text{and Ni}$) photocatalysts have been synthesized by solid state method for 12 hours at 900°C . $\text{M-doped CaBiO}_2\text{Cl}$ semiconductor photocatalysts show better crystallinity with the more compact and closer arrangement of brick-like particles in comparison with pure CaBiO_2Cl , showing higher photocatalytic activity for the decomposition of MB solution. Ni-doped CaBiO_2Cl is the best visible-light photocatalyst among all three metal modified CaBiO_2Cl catalysts studied here and the corresponding degradation rate of MB is about 95.3% after 140 min visible-light irradiation. $\text{M-modified CaBiO}_2\text{Cl}$ calcatalysts with smaller band gap widths broaden the absorption of visible light range. Furthermore, metal ions can act as trap sites and capture photogenerated electrons, which suppressed the recombination of electron-hole pairs and should be positive for the enhancement in photocatalytic activity.

Acknowledgments

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