Self-Propagating Combustion Synthesis of Ba4In2O7 and Its Photocatalytic Properties (Postprint)

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Abstract

$Ba(NO_3)_2$ and $In(NO_3)_3$ were used as starting materials, with glycine as fuel, to prepare tetragonal $Ba_4In_2O_7$ via self-propagating combustion synthesis. The samples were characterized by X-ray diffraction (XRD), thermogravimetric-differential thermal analysis (TG-DTA), UV-visible diffuse reflectance spectroscopy (UV-vis DRS), and nitrogen adsorption-desorption isotherms (BET) to investigate the influence of synthesis conditions on product formation and properties. Using Rhodamine B (RhB) as a degradation model, the effects of calcination temperature (T), calcination time (t), barium-to-indium molar ratio (Ba/In), glycine-to-metal ion molar ratio (G/M), and initial RhB concentration on the photocatalytic performance of the samples were studied. The results show that $Ba_4In_2O_7$ synthesized under conditions of T=800°C, t=1 h, Ba/In=2:1, and G/M=2:1 possesses a tetragonal crystal structure, high purity, and excellent photocatalytic activity. Effective degradation of a 5 mg/L RhB solution was achieved upon irradiation with a high-pressure mercury lamp (125 W) for 3 h, with a decolorization rate of 96.5%, and the degradation process follows a first-order kinetic model.

Full Text

Self-propagating Combustion Synthesis of $Ba_4In_2O_7$ and Its Photocatalytic Activity

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Abstract

Tetragonal $Ba_4In_2O_7$ compounds were synthesized via self-propagating combustion synthesis using $Ba(NO_3)_2$, $In(NO_3)_3$, and glycine as raw materials. The effects of synthesis conditions on the formation and photocatalytic activity of the compounds were investigated. The synthesized $Ba_4In_2O_7$ was characterized by X-ray diffraction (XRD), thermogravimetric analysis-differential thermal analysis (TG-DTA), UV-visible diffuse reflectance spectroscopy (UV-vis DRS), and N_2 adsorption-desorption isotherms (BET). Using rhodamine B (RhB) as a model degradation compound, the effects of calcination temperature (T), calcination time (t), Ba to In molar ratio (Ba/In), glycine to metal ion molar ratio (G/M), and the initial concentration of RhB on the photocatalytic activity of $Ba_4In_2O_7$ were investigated.

The results show that the synthetic $Ba_4In_2O_7$, prepared under conditions of T=800°C, t=1 h, Ba/In=2:1, and G/M=2:1, exhibits a tetragonal structure, high purity, and excellent photocatalytic activity. RhB (5 mg/L) can be completely decomposed in 3 h under illumination from a high-pressure mercury lamp (125 W), and the decolorization rate of RhB can reach 96.5%. The degradation process follows the first-order kinetic model.

Keywords inorganic non-metallic materials, $Ba_4In_2O_7$, photocatalysis, self-propagating combustion synthesis, rhodamine B

Introduction

In 1989, Lalla and Müller-Buschbaum synthesized $Ba_4In_2O_7$ via high-temperature solid-state reaction, which belongs to the tetragonal crystal system with unit cell parameters a=b=0.4175 nm and c=2.9483 nm. The crystal structure consists of two $[InO_5]^{2-}$ two-dimensional polyhedra separated by two $[BaO_2]$ layers along the c-axis, where the In^{3+} in the $[InO_5]$ polyhedra can be substituted by other trivalent metal ions. Gołąb et al. investigated rare-earth-doped $Ba_4In_2O_7$ prepared by high-temperature solid-state method, synthesizing Er-$Ba_4In_2O_7$ and Nd-$Ba_4In_2O_7$ compounds where Er^{3+} and Nd^{3+} replaced In^{3+} at the center of the polyhedra. Wang et al. prepared Cr-doped $Ba_4In_2O_7$ and Cr-In_2O_3 via sol-gel method for use in hydrogen storage alloy photoelectrodes, which exhibited good photo-assisted chargeability under xenon lamp irradiation.

Self-propagating combustion synthesis (SHS), also known as combustion synthesis (CS), has been extensively studied as an alternative to solid-state methods. Compared with conventional solid-state reactions, SHS requires neither high reaction temperatures nor long reaction times, and can avoid hard agglomeration and grain growth during high-temperature calcination. In this work, we prepared $Ba_4In_2O_7$ via self-propagating combustion synthesis using $Ba(NO_3)_2$ and $In(NO_3)_3$ as starting materials with glycine as fuel. We investigated the preparation conditions for tetragonal $Ba_4In_2O_7$ and examined the effects of calcination temperature (T), calcination time (t), Ba/In molar ratio, glycine to metal ion molar ratio (G/M), and initial RhB concentration on the formation and photocatalytic performance of $Ba_4In_2O_7$ samples.

1. Experimental

1.1 Preparation of $Ba_4In_2O_7$ Appropriate amounts of $Ba(NO_3)_2$, $In(NO_3)_3$, and glycine were dissolved in deionized water and heated with magnetic stirring. When the solution volume had evaporated to half, it was transferred to a crucible. The crucible was placed in a muffle furnace and heated to 200°C at 5°C/min, held for 30 min, then further heated to 400°C at 2°C/min and held for 30 min to allow complete self-propagating combustion. Finally, the combustion product was heated to 800°C at 10°C/min, maintained for 1 h, and naturally cooled to room temperature. The resulting powder was ground to obtain the $Ba_4In_2O_7$ sample.

1.2 Sample Characterization The crystal structure of samples was characterized using an XRD-7000s X-ray diffractometer (XRD) with Cu Kα radiation over the 2 range of 10°–80°. Specific surface area was measured using a JK-BK122W static nitrogen adsorption instrument. UV-visible diffuse reflectance spectra (UV-vis DRS) were recorded on a TU-1901 double-beam UV-visible spectrophotometer using $BaSO_4$ as reference. Thermal stability was analyzed using a ZCT-B thermogravimetric-differential thermal analyzer.

Photocatalytic performance evaluation was conducted in a custom-built photocatalytic reactor consisting of a light source (high-pressure mercury lamp, 125 W), quartz test tube (length 22.0 cm, diameter 2.0 cm, positioned 10 cm from the light source), light source cooler, and air inlet tube. During photocatalytic reactions, air was bubbled through the bottom of the quartz tube at 200 mL/min to maintain catalyst suspension. In a typical experiment, 50 mL of 5 mg/L RhB solution and a certain amount of photocatalyst were added to the quartz reactor. After 30 min of air bubbling in the dark, the light source was turned on and timing began. Samples were collected at intervals, centrifuged at high speed, and the supernatant absorbance was measured at 554 nm. Photocatalytic performance was evaluated based on the ct/c_0 ratio, where c_0 is the initial concentration (mg/L) and ct is the concentration at reaction time t (mg/L).

2. Results and Discussion

2.1 Characterization Results The XRD pattern of $Ba_4In_2O_7$ synthesized at T=800°C, t=1 h, and Ba/In=2:1 is shown in [Figure 1: see original paper]. The sample exhibits distinct diffraction peaks at 11.92° (210), 24.30° (421), 25.97° (422), 30.14° (440), 38.80° (640), 39.88° (642), 43.23° (008), 51.17° (664), 53.54° (844), 62.68° (880), and 71.19° (1240). These characteristic peaks match perfectly with those of $Ba_4In_2O_7$ (JCPDS No. 49-0891, a=b=0.4175 nm, c=2.9483 nm) without any impurity peaks, confirming the formation of high-purity tetragonal $Ba_4In_2O_7$. The sharp and well-defined diffraction peaks also indicate good crystallinity of the $Ba_4In_2O_7$ sample.

The UV-vis DRS spectrum of $Ba_4In_2O_7$ is presented in [Figure 2: see original paper]. The sample shows absorption across the entire spectral range, particularly strong absorption between 200–450 nm, demonstrating good UV-visible absorption capability. The band gap energy was determined using the Tauc plot method. The $(\alpha h\ )^2$ versus h curve is shown in the inset of [Figure 2: see original paper], where α is the absorption coefficient and h is the photon energy. Extrapolating the linear portion of the curve to the x-axis yields the band gap energy, which was determined to be 2.58 eV for $Ba_4In_2O_7$.

[Figure 3: see original paper] shows the TG-DTA curves of the $Ba_4In_2O_7$ precursor (a mixture of $In(NO_3)_3$, $Ba(NO_3)_2$, and glycine) after heat treatment at 400°C. The TG curve reveals two continuous weight loss processes from 415.9°C to 655.5°C. The DTA curve shows one endothermic peak at 649.8°C and two exothermic peaks at 452.8°C and 515.4°C. The weight loss from 415.9°C to 507.3°C (approximately 11.52%) is attributed to glycine decomposition, while the loss from 507.3°C to 655.5°C (approximately 13.74%) corresponds to the formation of $Ba_4In_2O_7$ from the decomposition of $Ba(NO_3)_2$ and $In(NO_3)_3$. The endothermic peak at 649.8°C corresponds to the energy required for the reaction between intermediate $BaCO_3$ and In_2O_3 to form $Ba_4In_2O_7$. The exothermic peak at 452.8°C likely corresponds to the self-propagating combustion of glycine and decomposition of $In(NO_3)_3$ and $Ba(NO_3)_2$, while the peak at 515.4°C may represent energy released during the formation of intermediate $BaCO_3$ and In_2O_3. The mass remains essentially constant between 655°C and 900°C, with two weak exothermic peaks possibly corresponding to energy released during the final formation of $Ba_4In_2O_7$.

The N_2 adsorption-desorption isotherm of $Ba_4In_2O_7$ is shown in [Figure 4a: see original paper]. The nearly overlapping adsorption and desorption curves indicate a narrow and relatively uniform pore size distribution. The pore size distribution curve in [Figure 4b: see original paper] reveals an average pore diameter of 8.98 nm, with pores primarily distributed in the 2–16 nm range. The specific surface area of the $Ba_4In_2O_7$ sample was measured to be 10.97 m^2/g.

2.2 Effects of Synthesis Conditions

2.2.1 Effect of Calcination Temperature The influence of calcination temperature on $Ba_4In_2O_7$ formation and photocatalytic activity was investigated under conditions of Ba/In=2:1 and t=1 h. As shown in [Figure 5: see original paper], at T=500°C, the diffraction pattern matches $Ba(NO_3)_2$ with minor impurity peaks of $BaCO_3$ (2 =23.9°, 24.3°, and 41.98°) and In_2O_3 (2 =30.58°, 51.03°, and 60.67°). At T=600°C, the sample consists mainly of $BaCO_3$ and

In_2O_3. At T=700°C, the main peaks correspond to $Ba_4In_2O_7$ but with accompanying $BaCO_3$ impurity peaks. At T=800°C, the diffraction peaks match perfectly with $Ba_4In_2O_7$ without any impurity phases. At T=900°C, although the main peaks remain consistent with $Ba_4In_2O_7$, peak broadening indicates grain growth. These results demonstrate that $Ba_4In_2O_7$ does not form below 700°C; at 700°C it forms but with impure composition; temperatures exceeding 900°C cause particle agglomeration. Only at 800°C does the synthesis produce pure, high-purity tetragonal $Ba_4In_2O_7$.

The photocatalytic degradation curves for $Ba_4In_2O_7$ synthesized at different calcination temperatures are shown in [Figure 6: see original paper]. In the absence of light, $Ba_4In_2O_7$ exhibits some adsorption capacity (14.1% adsorption after 3 h), attributed to its porous surface. Under high-pressure mercury lamp irradiation, the $Ba_4In_2O_7$ calcined at 800°C shows the best photocatalytic performance.

2.2.2 Effect of Calcination Time The effect of calcination time on $Ba_4In_2O_7$ formation and photocatalytic activity was examined at Ba/In=2:1 and T=800°C. [Figure 7: see original paper] shows that when t$ 1h, thediffractionpeaksmatchBa{4}In{2}O_{7}$ perfectly, but the peak intensity decreases with prolonged calcination time. This indicates that during calcination, the starting materials react to form $Ba_4In_2O_7$ particles that gradually grow into complete crystals. However, further extending the calcination time leads to agglomeration of well-developed $Ba_4In_2O_7$ particles, resulting in larger particle sizes (see) and smaller specific surface areas, ultimately causing decreased photocatalytic performance. As shown in [Figure 8: see original paper], the photocatalytic activity of $Ba_4In_2O_7$ decreases with increasing calcination time, with optimal activity achieved at 1 h.

2.2.3 Effect of Ba/In Molar Ratio The influence of the Ba/In molar ratio in the precursor on $Ba_4In_2O_7$ formation and photocatalytic activity was investigated at T=800°C and t=1 h. [Figure 9: see original paper] reveals that at Ba/In=1:1, the sample is primarily a mixture of $BaCO_3$ and In_2O_3. At Ba/In=1.5:1, characteristic $Ba_4In_2O_7$ peaks appear with In_2O_3 impurity peaks. At Ba/In=2:1, the diffraction peaks match $Ba_4In_2O_7$ perfectly. At Ba/In=2.5:1, the pattern shows $Ba_4In_2O_7$ peaks with minor $BaCO_3$ impurities. These results indicate that when the Ba/In ratio is below stoichiometric, insufficient Ba prevents complete reaction; when above stoichiometric, unreacted Ba remains as $BaCO_3$. As shown in [Figure 10: see original paper], the optimal photocatalytic activity is achieved at Ba/In=2:1, which was selected as the ideal molar ratio.

2.2.4 Effect of Fuel Amount The effect of glycine amount on $Ba_4In_2O_7$ formation and photocatalytic activity was studied at Ba/In=2:1, T=800°C, and t=1 h. Self-propagating combustion synthesis utilizes the chemical reaction between fuel and metal nitrates to convert nitrates to oxides or carbonates using thermal energy. Therefore, the fuel content in the precursor affects the combustion temperature and duration, influencing phase formation. [Figure 11: see original paper] shows XRD patterns of samples with different glycine to metal cation molar ratios (G/M). At G/M=1:1, the sample is a mixture of $Ba_4In_2O_7$, $BaCO_3$, and In_2O_3. At G/M=2:1, well-crystallized $Ba_4In_2O_7$ is obtained. At G/M=4:1, the sample consists of $BaCO_3$ and In_2O_3. Therefore, G/M=2:1 was selected for this study.

2.2.5 Effect of Initial RhB Concentration [Figure 12: see original paper] shows the degradation curves for RhB with different initial concentrations over $Ba_4In_2O_7$. The linear relationship between $\ln(c_0/c)$ and t for all concentrations follows first-order kinetics. The kinetic equations and parameters are listed in .

The photocatalytic degradation of RhB by $Ba_4In_2O_7$ prepared under optimal conditions is shown in [Figure 13: see original paper]. With increasing irradiation time, the main absorption peak of RhB in the visible region gradually decreases, and the UV region absorption peak also disappears. After 180 min, the decolorization rate reaches 96.5%. The degradation follows first-order kinetics with a rate constant k of 1.83$×10^{-2}$ mg·$(L \cdot min)^{-1}$ and half-life $t_1/_2$=37.8 min. Notably, the main absorption peak position remains unchanged during degradation, indicating that the chromophoric groups (phenylamino and carbonyl bonds) in RhB are gradually destroyed. The solution color changes from pink to colorless, demonstrating complete mineralization. Under the same conditions, a comparative experiment using a xenon lamp (150 W) with a JB400 nm filter (cutting off light below 400 nm) achieved only 41.8% decolorization after 180 min of visible-light photocatalysis.

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3. Conclusion

Tetragonal $Ba_4In_2O_7$ can be prepared by self-propagating combustion synthesis using $Ba(NO_3)_2$ and $In(NO_3)_3$ as starting materials with glycine as fuel. Calcination temperature, calcination time, precursor Ba/In molar ratio, and glycine dosage all influence the composition and photocatalytic performance of $Ba_4In_2O_7$. Under optimal conditions of 800°C calcination temperature, 1 h calcination time, Ba/In molar ratio of 2:1, and glycine to metal ion molar ratio of 2:1, the prepared $Ba_4In_2O_7$ exhibits a tetragonal crystal structure with high purity and excellent UV photocatalytic activity. Irradiation with a high-pressure mercury lamp (125 W) for 3 h achieves 96.5% decolorization of RhB, with degradation following first-order kinetics (k =1.83$×10^{-2}$ mg·$(L \cdot min)^{-1}$, $t_1/_2$=37.8 min).

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