Ternary Wide Band Gap p-Block Metal Semiconductor ZnGa$_4$O$_7$ for Photocatalytic Benzene Degradation

Zhaohui Li*, Hun Xue, Ling Wu, Xuxu Wang, Xianzhi Fu*
State Key Laboratory Breeding Base of Photocatalysis, Fuzhou University, Fuzhou 350002, P. R. China;
*E-mail: zhaohuili1969@yahoo.com; xzfj@fzu.edu.cn

Introduction

Benzene is a widespread environmental pollutant. Although TiO$_2$-based photocatalytic oxidation (PCO) has been established to be one of the most promising technologies for the environment remediation, PCO meets with limited success in the treatment of aromatic compounds like benzene due to the deactivation of TiO$_2$ resulted from the accumulation of the stable reaction intermediates on the surface. The development of new photocatalysts with high performance for benzene degradation is indispensable.

Our recent studies have shown that some wide band gap p-block metal semiconductors like Ga$_2$O$_3$, In(OH)$_3$, InOOH and Sr$_2$Sb$_2$O$_7$ [1] show high activity and stability in the photocatalytic degradation of benzene. The high photocatalytic performance observed over these wide band gap p-block metal semiconductors is related to their peculiar electronic structure. However, the already known wide band gap p-block metal semiconductor photocatalysts are limited. Besides this, except the common characteristics like wide band gap and the dispersive conduction band, other factors influencing their photocatalytic activity remain largely unclear. To study these influencing factors, more wide-band gap p-block metal semiconductors, especially those ternary ones, due to their diversified crystallographic and electronic structure, and their photocatalytic activity should be investigated.

Herein we reported the preparation of nanocrystalline ZnGa$_4$O$_7$ via a co-precipitation method and the study of its photocatalytic activity for benzene degradation. The as-prepared ZnGa$_4$O$_7$ showed superior photocatalytic activity and stability for benzene degradation to commercial TiO$_2$. However, its activity is lower as compared to another ternary wide band gap p-block metal semiconductor photocatalyst Sr$_2$Sb$_2$O$_7$. The difference of the photocatalytic activity between ZnGa$_4$O$_7$ and Sr$_2$Sb$_2$O$_7$ can be well explained by their different geometric structures.

Materials and Methods

Nanocrystalline ZnGa$_4$O$_7$ was prepared by a co-precipitation method. Aqueous solutions of Zn(NO$_3$)$_2$·6H$_2$O and Ga(NO$_3$)$_3$·xH$_2$O were mixed in the molar ratio of 1:2. Under vigorous stirring, ammonia solutions were dropped simultaneously into the mixed nitrate solutions until the pH value was in the range of 7–8. Then the precipitate slurry was thoroughly stirred. The precipitate was separated, washed with distilled water and absolute ethanol for several times. The precipitation obtained was dried in air at 80 °C, and then ground and sintered at 600 °C for 5 h in air.

The photocatalytic degradation of benzene was conducted in a tubular quartz micro-reactor operating in a continuous-flow mode under 254 nm UV illuminations. The initial benzene concentration was 220 ppm.

Results and Discussion

The XRD of the as-prepared sample indicates the formation of the pure phase of ZnGa$_4$O$_7$ (Figure 1). Figure 2 shows the conversion of benzene and the amount of produced CO$_2$ over the as-prepared ZnGa$_4$O$_7$ and P25 as a function of illumination time. The benzene conversion over ZnGa$_4$O$_7$ was about 12.0% and more than 100 ppm of CO$_2$ was produced, which corresponds to a high mineralization ratio of about 63%. The high conversion and mineralization ratio can be maintained for more than 20 h.

Although the photocatalytic performance for benzene degradation over ZnGa$_4$O$_7$ (12%) is superior to that over P25, it is lower than that of Sr$_2$Sb$_2$O$_7$ (24%). The order of the photocatalytic activity between Sr$_2$Sb$_2$O$_7$ and ZnGa$_4$O$_7$ cannot be explained by their BET specific surface area (36.7 m$^2$/g for ZnGa$_4$O$_7$ and 4.2 m$^2$/g for Sr$_2$Sb$_2$O$_7$). The crystallographic structure analyses of ZnGa$_4$O$_7$ and Sr$_2$Sb$_2$O$_7$ reveal that the geometric structure of the interior polyhedra in these two semiconductors is different. In ZnGa$_4$O$_7$, the GaO$_6$ octahedron is normal without any distortion. However, in Sr$_2$Sb$_2$O$_7$, one type of SbO$_6$ is an elongated octahedron with two longer Sr–O bonds compared to the remaining four bonds with the same bond length, while the other type is a compressed octahedron with two shorter Sr–O bonds. This difference in the geometric structure may explain the different photocatalytic activity between Sr$_2$Sb$_2$O$_7$ and ZnGa$_4$O$_7$. This result indicates that the distortion of the interior polyhedra is probably favorable for the photocatalytic activity.

The photocatalytic oxidation of C$_6$H$_6$ and the amount of produced CO$_2$ over the nanocrystalline ZnGa$_4$O$_7$ as a function of reaction time, with TiO$_2$ (P25) as references. (△) (●) the conversion of C$_6$H$_6$ over the ZnGa$_4$O$_7$ and TiO$_2$ respectively, (●) (○) the amount of produced CO$_2$ over the ZnGa$_4$O$_7$ and TiO$_2$ respectively.

Significance

This study reveals that the crystallographic structure can influence the photocatalytic activity of these wide band gap p-block semiconductors. This study gives some new insights in the development of new ternary wide band gap p-block semiconductor photocatalysts for benzene degradation.

References