Supplementary Materials

One-Pot Hydrothermal Synthesis of La-Doped ZnIn$_2$S$_4$ Microspheres with Improved Visible-Light Photocatalytic Performance

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1. Experimental Section

Photocatalytic Experiments

Photodegradation experiments were carried out using homemade equipment, as seen in Figure S1. Three daylight lamps (30 W for each, $\lambda \geq 400$ nm) were designated as the visible-light source for triggering the photodegradation reaction. The dish filled with methyl orange (MO) or tetracycline hydrochloride (TCH) solution was placed under the daylight lamp, and the distance between the dish and the daylight lamp was about 10 cm. The light intensity was about 450 mW/cm$^2$. In a typical run, a thin layer of film (100 mg photocatalyst) was dispersed into the dish containing MO (60 mL, $4.0 \times 10^{-5}$ mol L$^{-1}$) or TCH (60 mL, 10 mg L$^{-1}$) aqueous solution. Prior to irradiation, the obtained suspension was stirred in the dark for 1 h to reach an adsorption-desorption equilibrium among the catalyst, MO (or TCH) and water. At given irradiating time intervals, 6 mL reacted solution was centrifuged to measure the concentration variation of MO (or TCH) solution by recording the variation of the intensity of absorption peak (464 nm for MO, and 357 nm for TCH) using an ultraviolet (UV)-visible spectrophotometer (TU1901, Puxi, China). The photodegradation of efficiency of MO (or TCH) under visible light irradiation was expressed by $C/C_0$, where $C$ is concentration of the MO (or TCH) solution at a certain irradiation time $t$, and $C_0$ is the initial concentration of MO (or TCH) solution after adsorption-desorption equilibrium.
2. Phase Structure and Composition

In our experiment, the tiny amount of La is mostly likely to form the phase of La$_2$S$_3$. The explanation is described as follows. In our work, no starting materials containing alkali (OH$^-$) or carbonate were introduced into the reaction system except a sulfur source. According to previous studies [1,2], other lanthanide-based compounds, such as La(OH)$_3$ and La$_2$O$_2$CO$_3$, could be formed in the presence of NaOH or (NH$_3$)$_2$CO. That is to say, no condition is satisfied to form La(OH)$_3$ or La$_2$O$_2$CO$_3$. On the other hand, it has been proved that some dopant ions, such as La$^{3+}$, Ce$^{3+}$, Gd$^{3+}$, Er$^{3+}$ or Y$^{3+}$, can be successfully introduced into ZnIn$_2$S$_4$[3,4]. Furthermore, no O1s X-ray photoelectron spectroscopy (XPS) peak was detected in the doped ZnIn$_2$S$_4$ sample. Based on above, it can be rationally inferred that La ions are mostly likely to substitute In ions to form the phase of La$_2$S$_3$.

3. Photocatalytic Performance

The color of the suspension continually became lighter with prolonging irradiation time, as shown in Figure S2.

![Figure S2](image)

**Figure S2.** The variation of color (methyl orange (MO)) during the photodegradation reaction over 1.5L-ZIS (1.5 at%_doped ZnIn$_2$S$_4$) catalyst.

References

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