

Hydrothermal synthesis and catalytic performances of a new series of photocatalyst $R_2Sn_2O_7$ ($R = Nd, Sm, Eu, Gd, Er, Yb$)

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Introduction

Recently, it has been confirmed that stannates showed high photocatalytic activity on decontamination, such as $CaSnO_3$ [1], $La_2Sn_2O_7$ [2], Zn_2SnO_4 [3]. These stannates consist of corner-shared SnO_6 octahedra in their crystal structures, and the bond angle of Sn-O-Sn is close to 180° . Thus, the photogenerated electron-hole pairs can migrate easily in the corner-shared framework of SnO_6 units. $R_2Sn_2O_7$ ($R = Nd, Sm, Eu, Gd, Er, Yb$) belongs to the family of Lanthanide stannates with a pyrochlore type structure. They act as potential panacea for the material research fields, such as magnetic frustration/spin ices, colossal magnetoresistance and superconductivity. However, their photocatalytic properties have not been reported. Among the synthetic methodologies for Lanthanide stannate, the hydrothermal synthesis is particularly promising in the preparation of complex oxides with high-quality and high surface areas. Therefore, we reported the synthesis of $R_2Sn_2O_7$ ($R = Nd, Sm, Eu, Gd, Er, Yb$) nanocrystals through a facile hydrothermal pathway. The as-prepared samples show different photocatalytic activity on the decomposition of methyl orange (MO) under 254 nm ultraviolet light irradiation.

Materials and Methods

Equal molar amounts of $Na_2SnO_3 \cdot 4H_2O$ and $R(NO_3)_3 \cdot xH_2O$ ($R = Nd, Sm, Eu, Gd, Er, Yb$) were put into a beaker and dissolved by deionized water. Under stirring, 4 mol/L NaOH was dropped into the solution to adjust the pH value to 13. The mixture was then loaded into a 100 mL Teflon-lined autoclave, filled with deionized water up to 70% of the total volume and sealed tightly. Then the autoclaves were kept at $180^\circ C$ for 24 h. After cooling to room temperature, the precipitates were collected, washed with distilled water and absolute ethanol several times, and then dried in air at $80^\circ C$.

Results and Discussion

Figure 1 shows the typical XRD patterns of the as-prepared samples. All the diffraction peaks could be readily indexed to the pure phase of $R_2Sn_2O_7$ ($Nd_2Sn_2O_7$, JCPDS-871220; $Sm_2Sn_2O_7$, JCPDS-880458; $Eu_2Sn_2O_7$, JCPDS-880457; $Gd_2Sn_2O_7$, JCPDS-130186; $Er_2Sn_2O_7$, JCPDS-871224; $Yb_2Sn_2O_7$, JCPDS-871226). No impurity peaks such as those of SnO_2 or $R(OH)_3$ were detected. Since they all have cubic crystal system with Fd-3m space group, the position of the main reflection peaks of the samples are similar. An expanded view of the peak corresponding to (2 2 2) plane shows that the diffraction peaks are slightly shifted to higher angles, when R is changed from Nd to Yb (Figure 2). Indeed, with the decreasing of ionic radius from Nd^{3+} to Yb^{3+} , the mismatch between R^{3+} to SnO_6 octahedra leads to the octahedral tilting distortion. As predicted by UV-Vis DRS spectra, the band gap is 3.94, 4.38, 4.74, 5.00, 5.05 and 5.11 eV for $R^{3+} = Yb^{3+}, Er^{3+}, Gd^{3+}, Eu^{3+}, Sm^{3+}$ and Nd^{3+} , respectively. The band gap decreases with decreasing R^{3+} radius.

Photocatalytic activities of the series of pyrochlore type stannates were evaluated by the degradation of MO. 0.1 g catalyst was used per 150 ml of MO solution (10 mg/L). In Figure 3, it is clear that all can effectively degrade MO, and the substitution of R^{3+} has a strong effect on the photocatalytic performances of $R_2Sn_2O_7$. As can be seen, when the R^{3+} decreases from Nd^{3+} to Yb^{3+} , the activity improves significantly. On one hand, with decreasing R^{3+} radius, dipole moments are generated in octahedral units because of the octahedral tilting distortion, which may facilitate the mobility of charge carriers and improve the activity of $R_2Sn_2O_7$. On the other hand, the narrower band gap caused by the decrease of R^{3+} radius suggests easier excitation for an electron from the valence band to the conduction band in oxide semiconductor, and hence results in higher photocatalytic activity. However, there is an exception for $Er_2Sn_2O_7$, which has the highest activity though the Er^{3+} radius is not the minimum. This may be ascribed to its large specific surface area and small particle sizes.

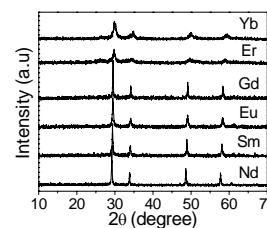


Figure 1

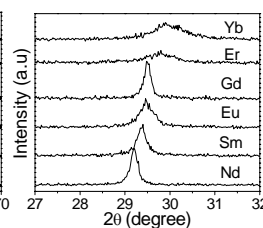


Figure 2

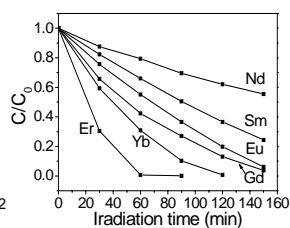


Figure 3

Figure 1 X-ray diffraction patterns of as-prepared $R_2Sn_2O_7$ ($R = Nd, Sm, Eu, Gd, Er, Yb$)

Figure 2 X-ray diffraction patterns of crystal plane (222)

Figure 3 Photocatalytic degradation of MO under $R_2Sn_2O_7$ ($\lambda = 254$ nm)

Significance

This work provides a series of Lanthanide stannates $R_2Sn_2O_7$ ($R = Nd, Sm, Eu, Gd, Er, Yb$) used as novel photocatalysts. The variation of R^{3+} radius in $R_2Sn_2O_7$ has a strong effect on crystal structure and photocatalytic properties. The study of modification of crystal structure by controlling the ionic radius in photocatalysts will provide useful information on making photocatalysts with high activity.

Acknowledgements

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