Stably Photocatalytic Decomposition of Rhodamine-B by Samarium Doped ZrO_2-ZnO Composite under Simulant Solar Light Irradiation

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Abstract. The Sm-ZrO_2-ZnO catalyst prepared by hydrothermal method is proved to be superior in stably photocatalytic degradation of Rhodamine-B under simulant solar light irradiation. Sm doping improves the ultraviolet and visible light absorbance. Composition of ZnO with ZrO_2 leads to enhancement of ultraviolet light absorbance, change of the ZnO morphology from nano-granule to rod and good dispersion of nano-ZrO_2 particles over ZnO rod surface. The last is regarded as key to keep stable activity for the catalyst. The high photocatalytic activity is ascribed to the p-n heterojunction formation and uniform distribution of fine ZrO_2 particles over ZnO. This morphology plays an import role in light absorption and enhances the separation of photo-generated electron-hole pairs.

Introduction

Heterogeneous photocatalysts, such as TiO_2, the most popular photocatalyst with an efficient electron transfer process, offer great potential for mineralization of organic pollutants [1,2]. Zinc oxide (ZnO) is another most promising photoactive oxides for decomposition of contaminants [3,4]. As a n-type semiconductor, ZnO presents unique characteristics, such as wide band gap (3.37 eV) in the near-UV spectral region [2,4], strong oxidation ability, good photocatalytic property and a large free-exciton binding energy (60 meV) [3]. Under a certain conditions, the performance of ZnO is superior to TiO_2 in quantum efficiency and photocatalytic activity [1]. However, the defects of ZnO include low utilization of solar energy, photocorrosion, low migration rate and high recombination rate of the photoelectron and hole pairs, which limit its application.

As a semiconductor, ZrO_2 has been considered as a photocatalyst in different chemical reactions due to its relatively wide band gap (5.1 eV) and low negative valence band potential [5]. Although ZrO_2 possesses characteristics of favorable chemical and thermal stability and surface acidity, it is only motivated by the light below wavelength of 250 nm. It is relatively rarely utilized in photocatalytic degradation of organics compared with TiO_2 and ZnO.

In order to improve the heterogeneous photocatalysis activity under UV/visible/solar illumination, considerable effort has to be exerted to improve the immigration of photo-induced charge carriers. Amoung these methods, metal doping and binary oxide photocatalyst system have gained much attention [6,7]. On the other hand, there have been studies indicated that the structural and morphology characteristics of ZnO and ZrO_2 play an important role in photocatalytic activity of the catalysts [8,9]. Consequently, it is significant to research the composition of ZnO and ZrO_2 doped with metal oxides about its morphology and granularity properties and the effect on photocatalytic performance. There has been rare researches about the composited and doped compounds.

Herein, ZrO_2-ZnO composite oxides was prepared via hydrothermal method and doped with samarium cations. The improvement of its stably activity in photocatalytic degradation of Rhodamine-B under simulant solar light irradiation was tested. The differences arise from the

composition and Sm doping in light absorbance, crystalline size and morphology were analyzed via UV–Vis diffuse reflectance spectra (UV–Vis DRS), X-ray diffraction (XRD) and scanning electron microscopy (SEM) and compared with pure ZrO_2 and ZnO prepared by the same hydrothermal method.

Materials and Methods

Catalyst Preparation

The catalyst was prepared by hydrothermal method. A certain amount of zinc acetate and zirconium oxychloride (molar ratio of Zr/Zn is 1:1), samarium nitrate, hexadecyl ammonium bromide (MDHB, 0.1 g) were dissolve into deionized water (15 mL) and mixed under vigorous stirring at room temperature for 30 min to form the solution. Then NaOH solution with concentration of 30% was added dropwise into the stirred solution to adjust the pH. After the pH reaching 10.0, the mixed solution was continuously stirred vigorously for 1 h and stirred slowly for 12 h. This solution was transferred into a high pressure reactor to retain 12 h at 160 °C. The mixed solution was centrifugalized after self-cooling of the pressure reactor. The precipitates was washed with ultrapure water and ethyl alcohol for three times and then dried at 80 °C overnight. The drying solid was porphyrized to get the catalyst.

Catalyst Evaluation

The photocatalytic activity of the prepared catalyst was evaluated by measuring the degradation rate of Rhodamine-B. A 350 W xenon short arc lamp (ShenZhen AnHongDa Opto Technology Co., Led.) with the similar characteristic spectrum with sun light was used as a light source. The 500 mg catalyst was added into 150 mL aqueous solution of Rhodamine-B with an initial concentration of 10 mg/L and the quartz reactor was sealed. After magnetically stirred for 30 min in the dark for adsorption/desorption equilibrium, the xenon lamp was turned on and the temperature of suspension was maintained at room temperature by circulation of water through an external cooling coil. At given intervals of illumination, a small amount of suspension was taken out and separated through high speed centrifugal separation to remove any catalyst particles. The concentration of the Rhodamine-B compounds in the filtrate was analyzed by ultraviolet-visible spectrophotometer (Shimadzu UV-2450) with wavelength of 525 nm. The percentage of Rhodamine-B removal efficiency was calculated by the equation: removal efficiency = $(C_0\text{-}C_e)/C_0\times100\%$, where C_0 and C_e (mg/L) are the concentrations of Rhodamine-B before and after light irradiation, respectively.

Characterizations

The crystalline phases and crystallite size of the catalysts were determined by X-ray diffractometer (Rigaku, D/Max 2500PC, Japan) in the 2θ angle range of 10–90º using Cu Kα radiation combined with nickel filter. Crystallite size was calculated according to Scherrer equation [10]. The UV–Vis DRS were recorded using a UV–Vis diffuse reflectance spectroscopy (UV-2540, Shimadzu, Japan) over the spectral range of 200–800 nm. Specific surface area were measured using a constant volume adsorption apparatus (Belsorp II, Bayer Japan Co., Ltd., Japan) through nitrogen adsorption at liquid nitrogen temperature (77 K) after degassing samples in vacuum at 120 °C for 3 h. The morphology of the catalysts was characterized by a scanning electron microscope (Hitachi S4700).

Results and Discussion

Recycle Performances of S_m-ZrO_2-ZnO

The effect of Zr/Zn molar ratio and doped amounts of Sm on catalytic activity has been investigated. The results show that the highest photcatalytic activity for Rhodamine-B degradation is obtained for a sample with Zr/Zn molar ratio of 1:1 and Sm doping amounts of 0.5 wt.%. Fig. 1 shows the activity of this optimal Sm-ZrO_2-ZnO catalyst for Rhodamine-B degradation in the successive cycles for photocatalytic reaction under simulant solar light irradiation. The catalyst was recycled by filtration

and wash with deionized water. The results show that the degradation ratio can reach to 99.3% after reaction for 60 min, indicating effectiveness for Rhodamine-B degradation. This optimal Sm-ZrO_2-ZnO catalyst is found to be active in the successive cycles for Rhodamine-B degradation, with successive removal efficiencies of 99.3%, 97.2%, 99.6%, 98.1% and 96.0% each time. Although it shows a little decline with reaction time, this decline in catalyst activity is due to the loss of the catalyst amounts during the process of filtration and wash. The result shows that Sm-ZrO_2-ZnO catalyst possesses good stability and it is not easy to lost its activation. It is known that photocorrosion is a problem for ZnO materials while ZrO_2 is chemical stable to has the better resistance to photocorrosion. Hence it is deduced that the composition of ZnO with ZrO_2 can protect unstable zinc ions from reaction with the photogenerated electron-hole. This is the reason for good stability of the Sm-ZrO_2-ZnO catalyst.

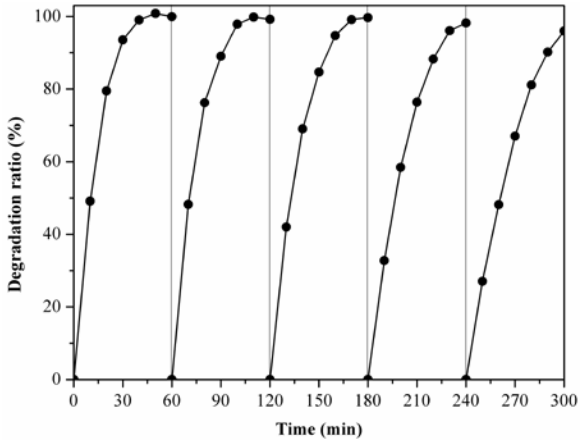

Fig. 1 Repeated runs for Rhodamine-B photodegradation with Sm-ZrO_2-ZnO under simulant solar light

UV-Vis DRS Analysis

The UV-Vis DRS of ZrO_2, ZnO, ZrO_2-ZnO (Zr/Zn=1:1) and Sm-ZrO_2-ZnO (0.5% Sm, Zr/Zn=1:1) are shown in Fig. 2. The absorption edge of ZrO_2-ZnO is at near 390 nm, close to that of ZnO and Sm-ZrO_2-ZnO. The combination of ZrO_2 with ZnO leads to obvious increase of the absorbance intensity in ultraviolet region of 250–390 nm compared with ZrO_2. The ZrO_2-ZnO presents stronger absorbance intensity of light response in ultraviolet region than ZnO, indicating the improvement of ultraviolet light absorption intensity by nano-ZrO_2. Sm doping plays a role in improving light absorption intensity in ultraviolet and visible region. It is deduced that the enhancement of light absorbance is one of the reasons for improvement of photocatalytic activity by recombination of ZnO and ZrO_2 and doped with Sm cations.

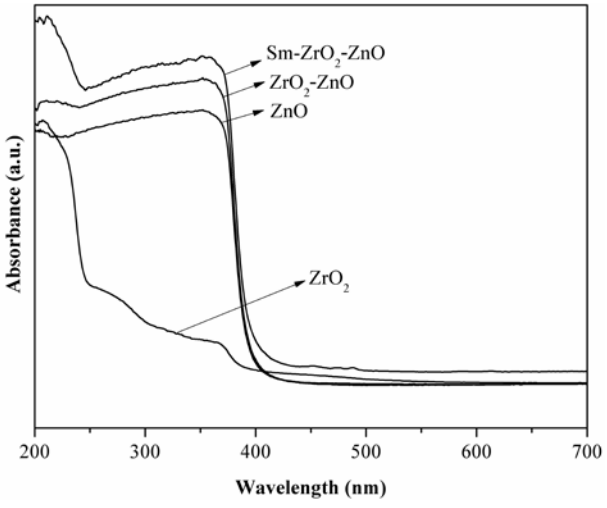

Fig. 2 UV–vis diffuse reflectance spectra of ZrO_2, ZnO, ZrO_2-ZnO and S_m-ZrO_2-ZnO

XRD Analysis

The crystal structure of ZrO_2, ZnO, ZrO_2-ZnO and Sm-ZrO_2-ZnO samples were examined by XRD, as shown in Fig. 3. The diffractograms reveal that ZrO_2 sample exhibits typical peaks of tetragonal *t*-ZrO_2 phase (major peaks at 2θ values of 30.27°, 35.25°, 50.37°, 60.21°, JCPDS No. 50-1089), and ZnO sample possess the hexagonal *h*-ZnO phase, presented at 2θ values of 31.77°, 34.42°, 36.25°, 47.54°, 56.60°, 62.86°, 67.96°, 69.10° (JCPDS No. 36-1451). The composite ZrO_2-ZnO and Sm-ZrO_2-ZnO samples present both the typical peaks of *t*-ZrO_2 and *h*-ZnO phases, inferring the existence of the ZrO_2-ZnO composite oxide, not solid solution. Based on the XRD results, the crystallite sizes of these powders were calculated using Scherrer equation. The crystallite sizes results and specific surface areas of these catalysts are listed in Table 1.

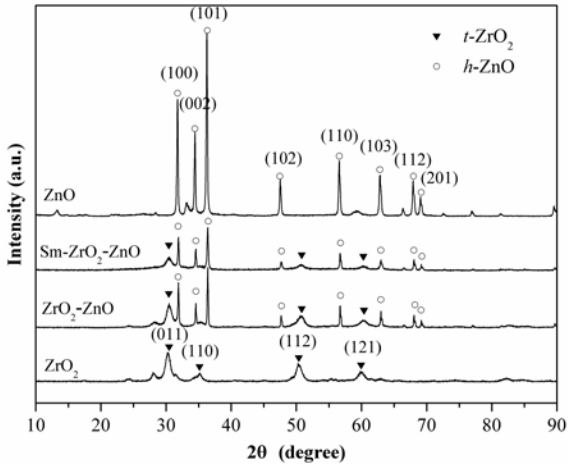

Fig. 3 XRD patterns of ZnO, ZrO_2 ZrO_2-ZnO (Zr/Zn=1:1) and S_m-ZrO_2-ZnO (0.5% S_m, Zr/Zn=1:1)

Table 1. Average crystal size and specific surface area of the catalysts

catalyst	ZrO_2	ZrO_2-ZnO	Sm-ZrO_2-ZnO	ZnO
Average crystal size of ZrO_2 [nm]	9.5	8.8	9.2	-
Average crystal size of ZnO [nm]	-	-	-	77.0
Specific surface area [m^2/g]	70.7	97.0	103.0	12.9

SEM Images

Fig. 4 shows the SEM micrograph for pure ZnO, ZrO_2, ZrO_2-ZnO and Sm-ZrO_2-ZnO catalysts. The images display that pure ZnO prepared by hydrothermal method are composed of numerous small granulates (Fig. 4a), pure ZrO_2 are floccule irregularly agglomerated by primary particles (Fig. 4b). It is interesting that the morphology of ZrO_2-ZnO composite is different with pure ZnO and ZrO_2. Fig. 4c and 4d show that morphology of ZnO changes to rods by composition with ZrO_2. The ZrO_2 rods in the composite possess widths of about 200–400 nm and ragged lengths of about 10–50 μm. The ZrO_2 attach to surface of ZnO rods as nano-particles which are smaller and more dispersive than pure ZrO_2. This is regarded as key to keep stable activity for the catalyst. It is inferred that p-n heterojunction is formed on contact interface between ZnO (n-type semiconductor) rods and fine ZrO_2 (p-type semiconductor) nano-grains. This heterojunction improves transformation of photogenerated electron-hole pairs and inhibits their recombination. The suitable size and uniform distribution of ZrO_2 particles over ZnO rods is in favor of light adsorption and then the transformation of photogenerated electron-hole pairs, resulting in promotion of photocatalytic degradation of the organics.

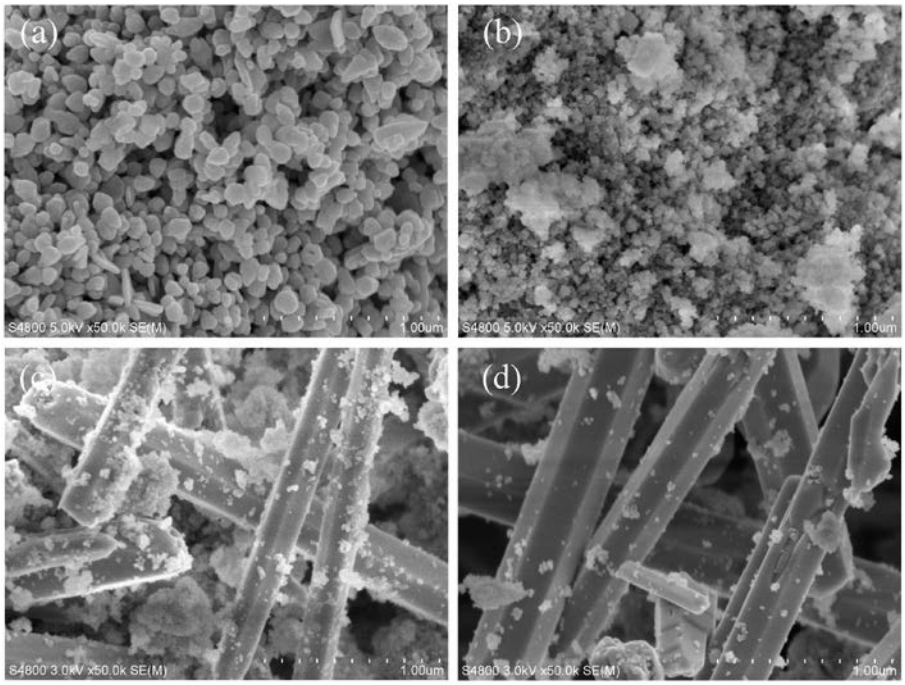

Fig. 4 SEM images for (a) ZnO; (b) ZrO_2 (c) ZrO_2-ZnO (Zr/Zn=1:1); (d) Sm-ZrO_2-ZnO (0.5% Sm, Zr/Zn=1:1)

Conclusions

In conclusion, the Sm-ZrO_2-ZnO catalyst prepared by hydrothermal method proved to be superior in stably photocatalytic degradation of Rhodamine-B under simulant solar light irradiation. The high photocatalytic activity is ascribed to the combined effects of the following two factors: (1) Composition of ZnO with ZrO_2 and doping with Sm lead to enhancement of ultraviolet and visible light absorbance; (2) Composition of ZnO with ZrO_2 leads to change of the ZnO morphology from granule to rod, smaller size of ZrO_2 grains and good dispersion of ZrO_2 fine particles over ZnO rods. This morphology and formation of p-n heterojunction play an import role in light adsorption and enhances the separation of photogenerated electron-hole pairs and inhibits their recombination. (3) The good dispersion of ZrO_2 fine particles over ZnO rods is regarded as key to keep stable activity for the catalyst.

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