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Photocatalytic Degradation of Rhodamine-B on Synthesized Nano-Hybrid CdS Catalyst

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In this paper, CdS/SBA-15 nano-hybrids are prepared by *in situ* synthesis method with the assistance of silane coupling agent. The catalyst was characterized using of XRD, FT-IR, TEM and N_2 adsorption-desorption. It was found that the CdS nanocrystals were confined in the channel of SBA-15. In addition, the prepared catalyst was used to photodegrade the rhodamine-B. Different catalytic conditions were investigated, the best degradation rate could reach 95 %.

Keywords: SBA-15, Silane coupling agent, Cadmium sulfide, Rhodamine-B.

INTRODUCTION

With the accelerating pace of industrialization and urbanization, the environmental pollution is a serious and growing problem throughout the world today, especially environmentally harmful wastewater with high levels of organic pollutants [1-3]. Photocatalytic oxidation technology shows advantages in wastewater treatment. Photocatalytic oxidation can make organic pollutants in wastewater been deep oxidation into inorganic pollution free, which has a higher degradation rate and a higher degree of mineralization [4,5]. It is well known that, nano CdS makes a great performance in photocatalytic [6-8]. With the change of band gap caused by quantum size effect, nanometer CdS can enhance its oxidation reduction ability. However, CdS applied into practice is difficult because its drawbacks of small specific surface area, difficult recovery and causing secondary pollution [9,10]. Therefore, preparing with a good photocatalytic performance which could overcome the disadvantages of CdS composite materials has practical significance.

Herein, we use mesoporous molecular sieve SBA-15 with large specific surface area and high thermal stability as a support, *in situ* synthesis of nanometer CdS in SBA-15 pore, then as-prepared photocatalyst are applied to the photocatalytic degradation of rhodamine-B.

EXPERIMENTAL

SBA-15 preparation: 4 g Triblock copolymer (P123) was added to 105 mL distilled water and then add 20 mL of 12 M HCl, the mixture was stirred at 40 °C by 3 h. Afterwards, dropwise 9.2mL tetraethyl orthosilicate (TEOS) under vigorous stirring within 10 min. Stirred for 4 h and then transferred into a Teflon-lined, stainless steel autoclave and aged at 110 °C for 24 h. Cool down to room temperature, the solid was filtered, washed repeatedly with deionized water and dried at room temperature. As-synthesized sample was calcined at 550 °C for 6 h.

SBA-15-CdS catalyst preparation: 0.5 g SBA-15 was added into Cd^{2+} solution [1.33 g $(CH_3COO)_2Cd{\cdot}2H_2O$ was dissolved in 50 mL methanol], stirring for 10 h. After been filtered, washed and dried, the precursor was followed by sulfuration with H_2S (hydrochloric acid reaction of ferrous sulfide and 1 mol/L) 10 h, the product was denoted as SBA-15-CdS.

Preparation of SBA-15-a-CdS and SBA-15-m-CdS: 1 g SBA-15 and 1.5 g silane 3-aminopropyl triethoxysilane was dissolved in 50 mL ethanol, after stirring for 24h under room temperature, after ultrasonic by ethanol (to avoid excess silane coupling agent adsorption). The filter was added into Cd^{2+} solution [1.33 g $(CH_3COO)_2Cd{\cdot}2H_2O$ was dissolved in 50 mL methanol], stirring for 10 h. After been filtered, ultrasonic by methanol (remove excess cadmium ion) and dried, the precursor was followed by sulfuration with H_2S 10 h, the products were denoted as SBA-15-a-CdS and SBA-15-m-CdS was prepared silane coupling agent replaced by methacrylic acid-3-(trimethoxysilyl)propyl in same method.

Characterization of samples: Powder X-ray diffraction (XRD) patterns were recorded in a Shimadzu XRD-6000 diffractometer system equipped with Ni-filtered Cu target K_α-ray (operation at 40 kV, 30 mA, wavelength $\lambda = 0.15418$ nm). Diffractions were carried out in the ranges (2θ) of 10° to 80° at the scanning speed of 4 °/min. Fourier transform infrared

(FT-IR) spectra of skeletal vibration of the materials were recorded using KBr disk in a SHIMADZU NICOLET AVATAR 370 DTGS spectrometer. N_2 adsorption/desorption isotherms were recorded at 77 K by a Micromeritics ASAP 2010. Before measurements, samples were outgassed at 573 K for 3 h. BET surface areas (S_{BET}) were calculated from adsorption-desorption isotherm in the relative pressure range from 0.05 to 0.30. Pore size distributions were calculated from adsorption-desorption isotherm by Barret-Joyner-Halenda (BJH) method. The surface area and pore volume were calculated by t-plot method. Transmission electron micrographs (TEM) were analyzed with a HITACHI H-8100 electron microscope operated at an accelerating voltage of 100 kV.

Photocatalytic degradation of rhodamine-B: The targeted degradation product was rhodamine-B solution. The experiment results showed that the concentration of rhodamine-B solution in the range of 5-20 mg/L was proportional to its UV absorbance (λ_{max} = 554 nm). The correlation between concentration, "C" and absorbency, "A", was fitted as follows:

$$C = 0.3745 + 8.4008\ A \quad (1)$$

Experimental light conditions: photodegradation reaction was in a closed environment of the homemade photocatalytic reactor, 250 W self-ballasted mercury lamp. Light from the reaction liquid level 10 cm. Add 100 mL rhodamine-B solution and the catalyst in reaction vessel, avoid light stirred for 0.5 h to reach the adsorption equilibrium of catalyst and then adjusted the pH value with 1M HCl. Then UV-irradiation started to initiate the photocatalysis reaction, samplings of the solution were drawn every 5 min, their absorbency were measured by a UV/visible spectrophotometer at the maximum absorptive wavemeter. Then according to Lambert-Bill's law, calculated the degradation rate:

$$\text{Degradation rate } (\%) = \frac{(A_0 - A_t)}{A_0} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

Fig. 1a show that prepared SBA-15 has the typical characteristic peak of SBA-15 (1.6° and 1.8°), which proves that the prepared carrier is SBA-15. After modified by 3-aminopropyl triethoxysilane, the peak value of SBA-15 is reduced significantly, because of amino-silane coupling agent destroy the pore structure of SBA-15 [4]. The three broadened peaks in Fig. 1b corresponds to (111), (220) and (311) lattice planes of cubic crystalline CdS, respectively [6].

The absorption peak of the carrier appeared in 3431 cm^{-1} (Fig. 2) can be attributed to the Si-OH stretching vibration of hydroxyl, due to the effect of silane coupling agent, the peak of Si-OH reduce [4], (c) and (d) approach to higher wave numbers in the peak. The band 1080 cm^{-1} belongs to the molecular sieves Si-O-Si antisymmetric stretching vibration, 952 cm^{-1} for Si-OH bending vibration 1620 cm^{-1} may be remnant template(P123) C=C stretching vibration caused by inadequacy calcinated, after modified by methacrylic acid-3-(trimethoxysilyl)propyl this peak rise (Fig. 2d). Because in the process of silane coupling of the Si-OH has been replaced with Si-O-Si, so here is to reduce peak, while 800, 465 cm^{-1} for the Si-O-Si symmetric stretching vibration and bending vibration [7].

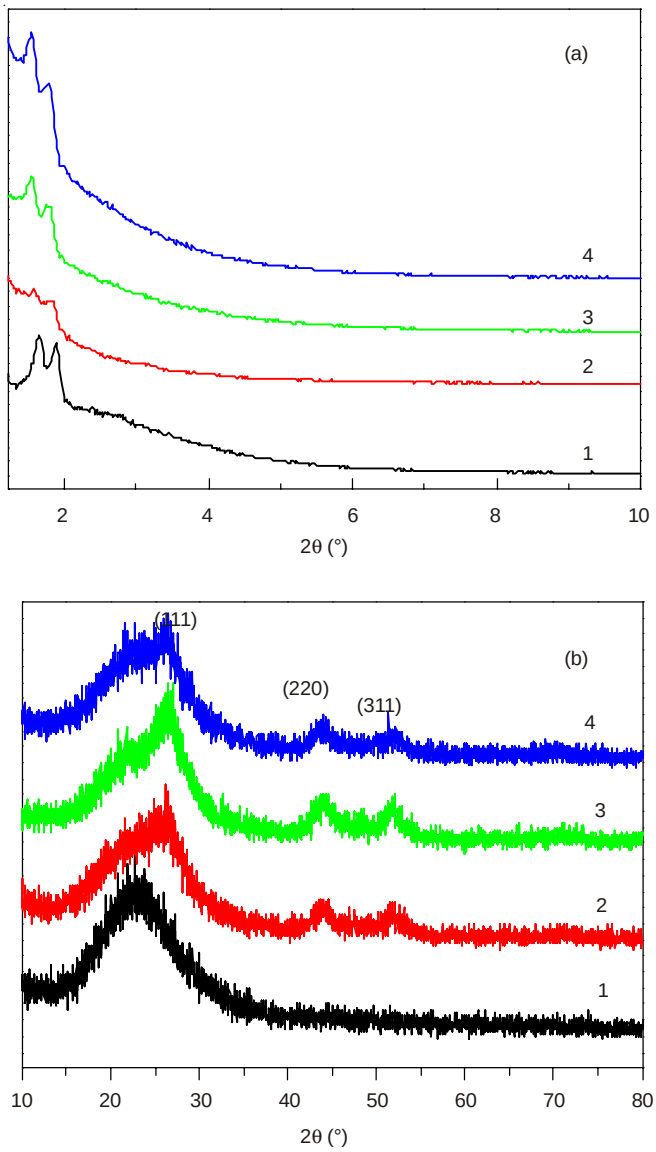

Fig. 1. Small (a) and wide (b) angle X-ray diffraction (XRD) patterns of the samples. SBA-15 (1). SBA-15-CdS (2). SBA-15-a-CdS (3). SBA-15-m-CdS (4)

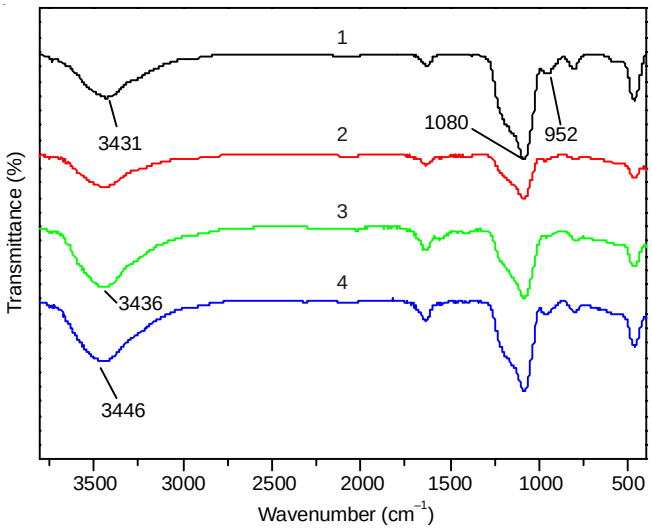

Fig. 2. Infrared spectroscopy (FT-IR) of SBA-15 (1). SBA-15-CdS (2). SBA-15-a-CdS (3). SBA-15-m-CdS (4)

As shown in Fig. 3a, it reveals that the highly ordered pore structure of SBA-15 has been preserved. It can clearly be seen that the CdS uniform distribution in SBA-15 molecular sieve channel (Fig. 3b, 3c and 3d). However, the SBA-15 molecular modified by 3-aminopropyl triethoxysilane can support more CdS particles because of SBA-15 molecular sieve surface is obviously damage (Fig. 3c).

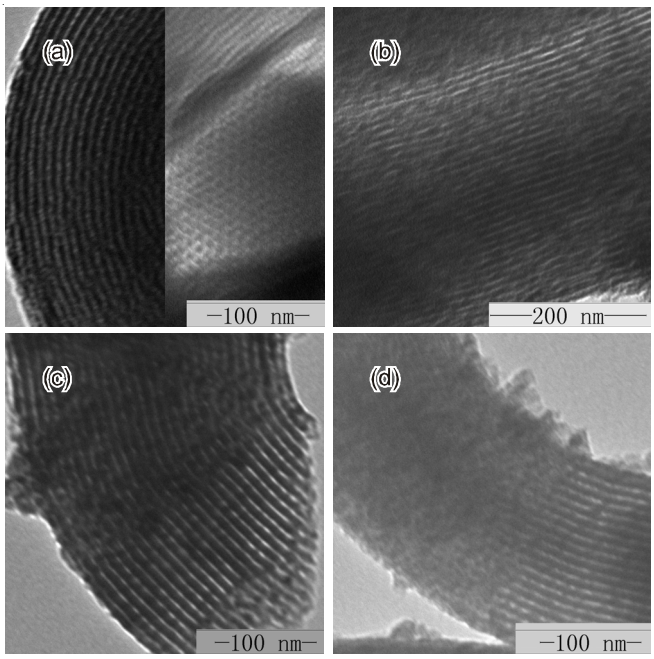

Fig. 3. Transmisson electron microscope (TEM) images of the samples. a, SBA-15. b, SBA-15-CdS. c, SBA-15-a-CdS. d, SBA-15-m-CdS

The specific surface area of SBA-15 is 722 m^2/g and mesoporous molecular sieve structure appear typical desorption hysteresis loop (Fig. 4a). In composite CdS-SBA-15, the channel of SBA-15 is occupied by cadmium sulfide, because the surface area relatively decreased and the corresponding loop was reduced. The specific surface area of SBA-15-m-CdS is 550 m^2/g, a relatively high reduction in SBA-15-a-CdS to 210 m^2/g. This shows that the SBA-15 modified by 3-aminopropyl triethoxysilane can support more CdS. The diameter of molecular sieve SBA-15 is 9.3 nm (Fig. 4b). After cadmium sulfide was added into SBA-15 channel, the diameter of pore decreases, the diameter of SBA-15-m-CdS is 7.6 nm and SBA-15-a-CdS is 6.4 nm.

The bad catalytic effect of SBA-15-a-CdS may due to low specific surface area and the catalytic effects of kinds of catalysts were high. Catalytic degradation rate of SBA-15-CdS was 92.5 % and that of SBA-15-m-CdS was 95.4 %. It showed that after modified by olefine acid- silane coupling agent, the composite catalyst can get better degradation effect.

Fig. 5b shows that the degradation rate of rhodamine-B was increased with the dosage of catalyst significantly. The degradation rate was 9 % when the dosage of catalyst was 0.1 g/L. When the dosage of catalyst 0.5 g/L, the degradation rate can be up to 95 % after illumination by Hg lamp 2 h, which was better than 0.7 g/L (81 %). It may be caused by agglomeration of catalyst decrease the catalytic activation.

Photodegradation rate of rhodamine-B effect by the solution concentration was not high. When the concentration of rhodamine-B was 20 mg/L, the degradation rate was 95 % (Fig. 5c).

As shown in Fig. 5d the pH value of the reaction system had great effect on the photocatalytic degradation of rhodamine-B solution, with the value pH increased. The degradation rate was decreased slightly, when the system pH = 2, the degradation rate can be up to 97.1 %; but when pH = 6, the degradation rate was also 80 %.

Catalyst SBA-15-m-CdS, catalyst dosage was 0.5 g/L, pH value of the system was 3 and the concentration of rhodamine-B was 20 mg/L, verifying 5 times of the optimum experimental conditions, the results were showed in the Table-1. It can be seen the perform of nano-hybrid CdS catalyst is very steady.

Conclusion

Preparation of SBA-15 mesoporous molecular sieve by hydrothermal synthesis method and the SBA-15 was modified with silane coupling agent. CdS nanoparticle was prepared by *in situ* synthesis inside SBA-15 aperture. Moreover the three kinds of CdS-SBA-15 catalysts were characterized by different means of XRD, FT-IR, TEM and N_2 adsorption-desorption techniques. The results showed that CdS was successfully loaded

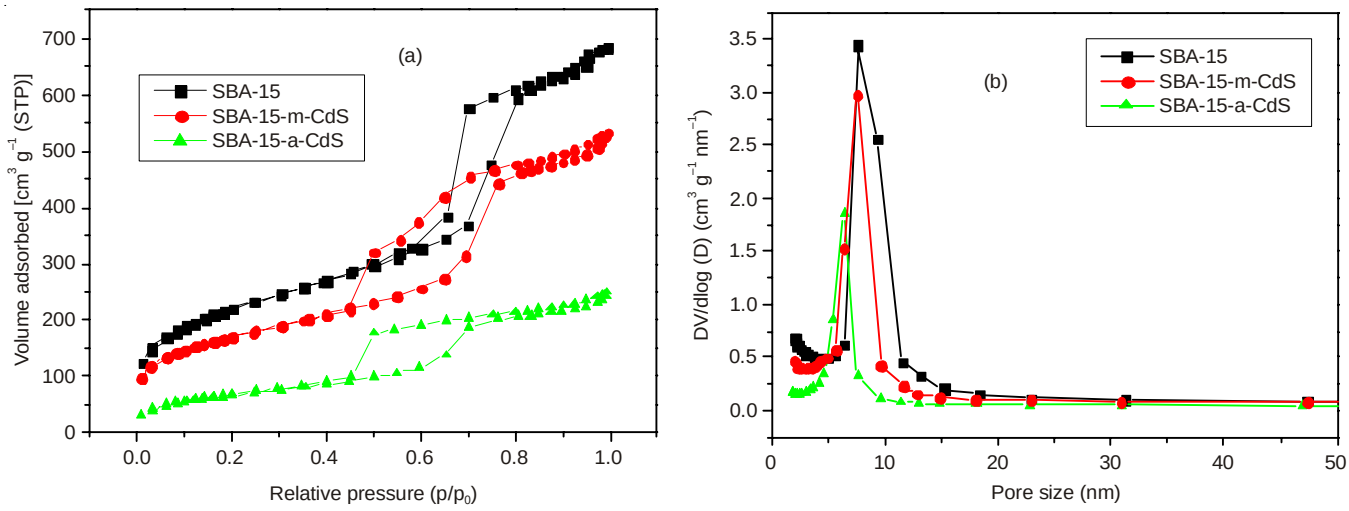

Fig. 4. N_2 adsorption-desorption isotherms (a) the pore size distribution (b) of the hierarchical porous aluminosilicate materials

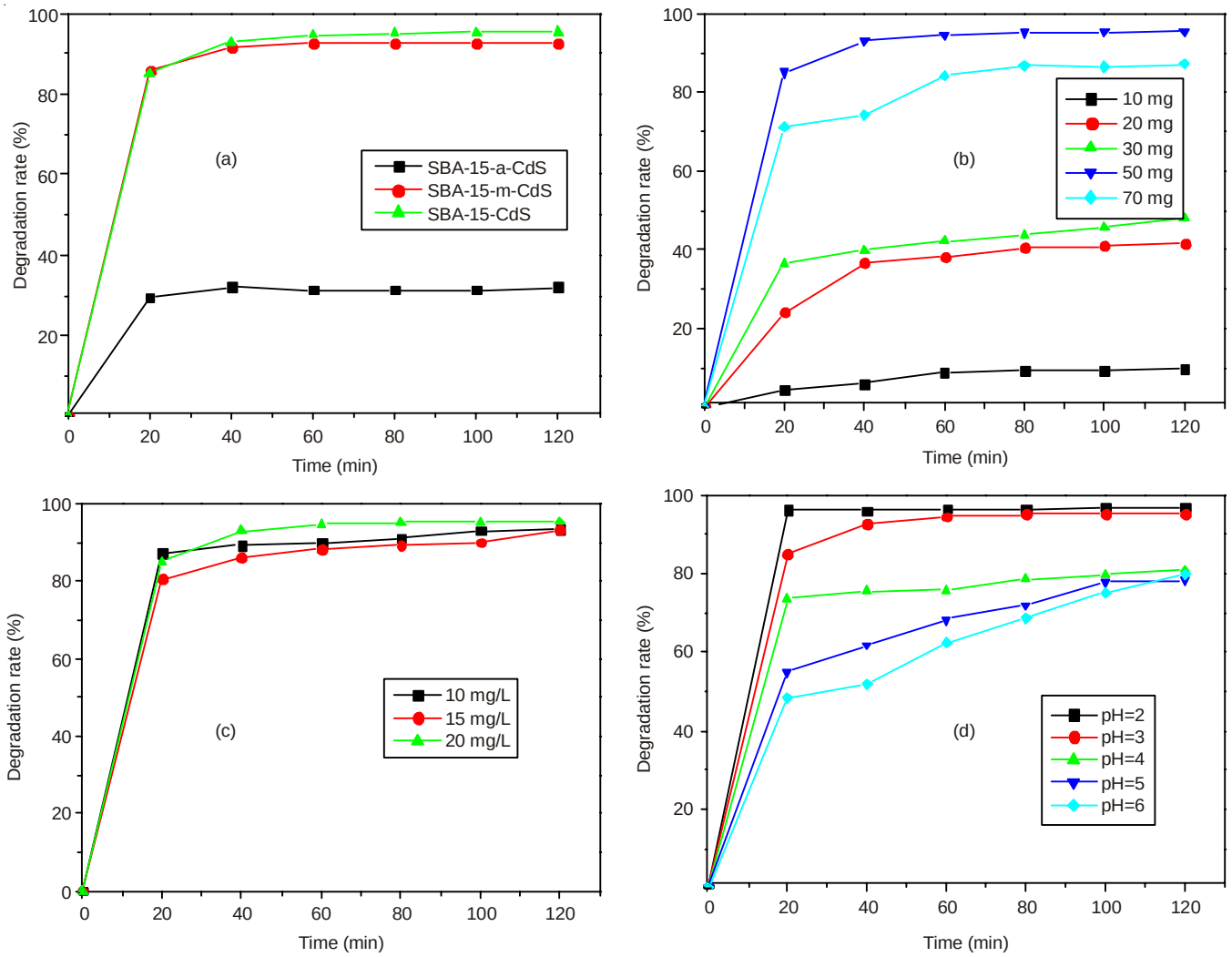

Fig. 5 (a) Effects of different catalyst on the degradation rate. (100 mL 20 mg/L degradation liquid, pH = 3 (adjust by 1 M HCl), the dosage of catalyst was 0.5 g/L,) (b) Effects of different catalyst dosage on the degradation rate. (100 mL 20 mg/L degradation liquid, pH = 3, catalyst SBA-15-m-CdS) (c) Effects of different concentration on the degradation rate. (100 mL 20 mg/L degradation liquid, pH = 3, the dosage of catalyst SBA-15-m-CdS was 0.5 g/L) (d) Effects of different pH value on the degradation rate. (100 mL 20 mg/L degradation liquid, the dosage of catalyst SBA-15-m-CdS was 0.5 g/L)

TABLE-1
VERIFY THE OPTIMUM EXPERIMENTAL CONDITIONS

Times of experiment	1	2	3	4	5	Average
Degradation rate (%)	93	94	94	96	95	94

on the SBA-15, amino-silane coupling agent can damage molecular sieve pore structure. After modified by olefine acid-silane coupling agent SBA-15-CdS nano-hybird photocatalytic degradation of rhodamine-B can achieve a degradation rate 95 %.

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