Degradation of rhodamine B using Cr-doped TiO_2 under visible light irradiation

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Abstract

In this study, the mesoporous Cr-doped TiO_2 powder was prepared using SDS as a surfactant by sol–gel method with the aim of extending the light absorption spectrum toward the visible light region. The photocatalytic activity under visible light irradiation was evaluated using rhodamine B as a model organic compound and was carried out in a recycle fluidized bed reactor. The effects of initial acid dye concentration, particle size and loading amounts of rhodamine B were investigated.

Keywords: Rhodamine B, Photocatalytic activity, Cr-doped TiO_2

1. Introduction

Dye pollutants produced from the textile industries are becoming a major source of environmental contamination. Traditional methods such as flocculation, carbon adsorption, reverse osmosis and activated sludge process have difficulties in the complete destruction of dye pollutants for the treatment of dye-containing [1-5]. In the past decades, scientists and engineers are all interested in developing the semiconductor photocatalytic reactions. TiO_2 has widely been investigated for photocatalyzed degradation of organic dyes because of its strong photoactive ability, stability, non-toxic and low cost. TiO_2 photocatalyst is well known to generate various active oxygen species such as hydroxyl radicals, hydrogen peroxide, superoxide radical anions, etc. by redox reactions under UV irradiation. It has been clarified that the photocatalytic activity of TiO2 strongly depends on its physical properties, such as crystal structure, surface area, particle size, surface hydroxyls, etc. [6-13]. Anatase-type of TiO_2 has highly photocatalytic activity for decomposition of various environmental pollutants in both gas and liquid phases.

However, TiO_2 can only utilize a small part (less than 5%) of the solar light energy for photocatalytic oxidation and the artificial UV light sources are unstable and expensive. In order to achieve photooxidation of pollutants with efficient utilization by titania particles under visible light irradiation, i.e., the band gaps must be smaller than 3.2 eV, the development of photocatalysts with high activity under visible light irradiation has been required. Thus for, extensive researches have been conducted to convert the TiO_2 absorption from the ultraviolet to the visible light region by the ion doping of transition metals [14]. Among these transition metal ions, Cr^{3+} has received much attention because its introduction can excellently extend the visible light absorption. In 2002, Palmisano et al. studied the photocatalytic degradation of aliphatic and aromatic compounds in aqueous systems on Cr-doped polycrystalline TiO_2 powder [15]. Afterwards, Gonzalez-Elipe et al. investigated the photocatalytic properties of Cr-doped TiO_2 thin film prepared by ion beam-induced CVD [16]. Zhang et al. studied the photooxidation of XRG (azoic dye) aqueous solution on Cr-doped TiO_2 prepared by a process that combined sol–gel with hydrothermal method. The results showed that Cr-doped TiO_2 effectively improved the photocatalytic activity under visible light irradiation within the optimal doping concentration from 0.15 to 0.2% [17]. Yin et al. synthesized the mesoporous Cr-doped TiO_2 and studied its electrorheological activity [18]. More recently, Yu et al. fabricated mesoporous Cr-TiO_2 photocatalyst and evaluated its activity for photodegradation of methylene blue. The results showed that the photocatalytic activity of mesoporous Cr-doped TiO_2 was higher than that of pure mesoporous TiO_2 [19]. However, so far, there is no systematic study on the effect of the Cr/Ti molar ratio on the acetaldehyde photodecomposition over mesoporous Cr-doped TiO_2 under visible light irradiation.

In present work, mesoporous Cr-doped TiO_2 was synthesized using SDS as a surfactant by sol–gel approach. The photocatalytic decomposition of rhodamine B over this obtained sample was conducted under visible light irradiation.

2. Experimental

2.1. Materials and methods

All of the Chemicals used in this work were analytical grade reagents and used without further purification. Deionized water was used to prepare all solutions.

XRD analysis was performed on a D Jeoljdx-8030 X-ray powder diffractometer with Cu K_{α} (l= 0.154 nm) radiation (40 kV, 30 mA). To estimate the average crystallite sizes of TiO_2 NPs, the Scherrerequation was applied. The particle morphologies of the as-prepared powders were observed by a Hitachi scanning electron microscopy (SEM) at 30 kV. The FT-IR analyses were carried out on a Shimadzu FTIR-8400S spectrophotometer using a KBrpellet for sample preparation. The DRS spectra were prepared via a Shimadzu (MPC-2200)spectrophotometer. For investigation of photocatalytic ability of nanocatalyst, the concentration of rhodamine B was determined spectrophotometrically using a double-beam UV-Visible spectrometer (ShimadzuUV-1700) at room temperature in the range of 200-800 nm.

2.2. Preparation of catalyst

In a typical synthesis, 3 ml of TBT was added to a solution containing 2 g of SDS and 12g of ethanol. To this solution, 1×10^{-4} mol $Cr(NO_3)_3$ was added for the synthesis of mesoporous Cr doped TiO_2 respectively. The resulting sol was gelled in an open petri dish at 50^0C in air for 4 days. The sample was calcined at 400^0C for 3 h in air at the heating rat of 2^0C/min to remove the surfactant.

2.3. Investigations of photocatalytic properties

100 ml of rhodamine B with a known initial concentration (5ppm) and 0.02g of the Cr-doped TiO_2 NPs were added to apyrex glass photoreactor. A 500W high-pressure Hg lamp (which the wavelength of its maximum intensity occurs in λ=546.8 nm) was used as light irradiation source. Reaction solution was sonicated for 4min to obtain a homogeneous suspension and then was magnetically stirred in the dark for 30 min to establish a rhodamine B adsorption /desorption equilibrium. During irradiation, the reaction medium was continuously purged with air at a constant flow rate to guarantee sufficient O_2 concentration in it. Samples of 3 ml were collected from supernatant solution every 30 minutes ones and immediately centrifuged at 14000 r/min for 20min. For investigation of photocatalytic ability of nanocatalysts, the concentration of rhodamine B was determined spectrophotometrically using a double-beam UV-Visible spectrometer (ShimadzuUV-1700) at room temperature in the range of 200-800 nm.

3. Result and discussion

3.1. Result of XRD

The powder XRD pattern (2θ range from 4° to 90°) of the synthesized Cr-doped TiO_2 sample is shown in Fig. 1. The diffraction peaks at 2θ = 25.33°, 37.75°, 47.95°, 54.13°, 62.72° corresponding to the anatase phase of titania (JCPDS, file No. 21-1272) are observed in the sample that displayed pure anatase phase.

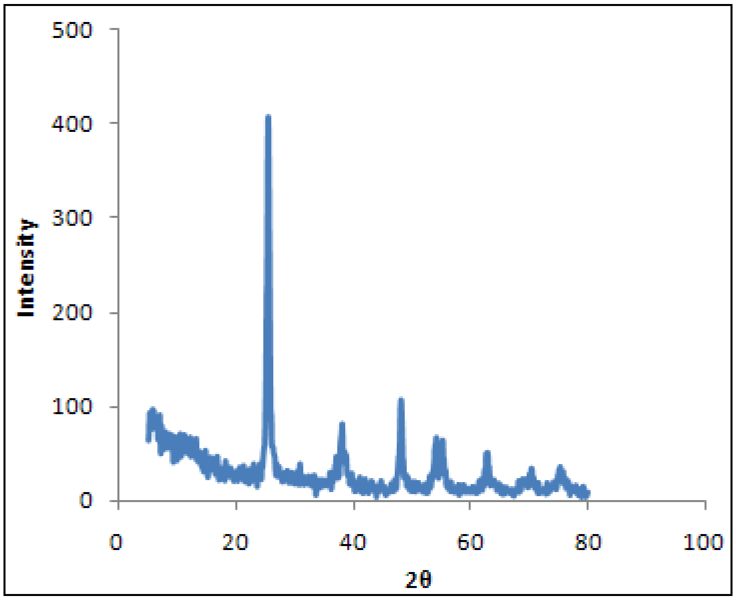

Fig. 1 XRD pattern of Cr-doped TiO_2 Photocatalyst

3.2. UV-Visible spectra

Figure 2 shows the UV–vis absorption spectra of mesoporous Cr-doped TiO_2. It is obvious that the doped Cr^{3+} can significantly improve the absorption of mesoporous TiO_2 in the visible light region. The absorption at wavelength of less than 387 nm is caused by the intrinsic band gap absorption of anatase TiO_2 (3.2 ev). The absorption around 450 nm is due to the charge transfer band $Cr^{3+} \rightarrow Ti^{4+}$ or $4A2g \rightarrow 4T1g$ of Cr^{3+} in an octahedral environment, and the broad absorption band from 620 to 800 nm is due to $4A2g \rightarrow 4T2g$ d–d transitions of Cr^{3+} With the increase in Cr^{3+} doping content, the absorption edge of mesoporous TiO_2 greatly extended into the visible light region. This extended absorbance indicates the possible enhancement in the photocatalytic activity of mesoporous TiO_2 illuminate by visible light.

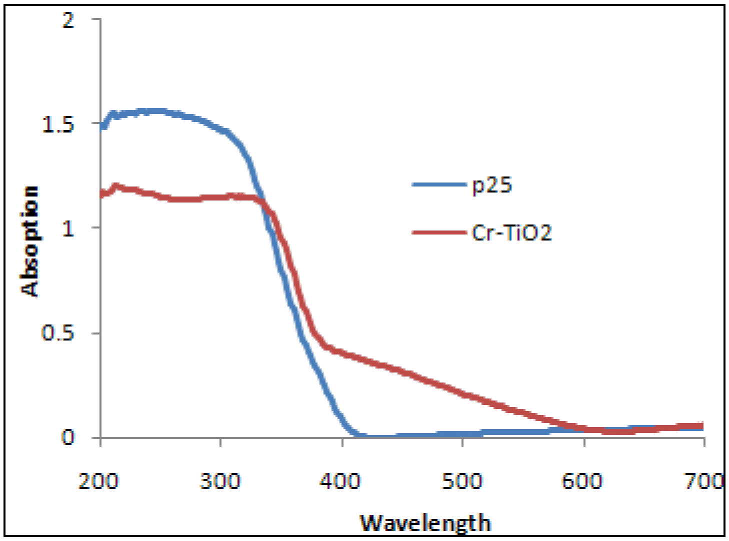

Fig. 2 UV-Vis diffuse reflectance spectra of Cr-doped TiO_2 Photocatalyst

3.3. Result of FT-IR

The FT-IR spectra of the sample indicated in Fig. 3. The band at 580-520 cm^{-1} was assigned to the Ti-O stretching vibration.

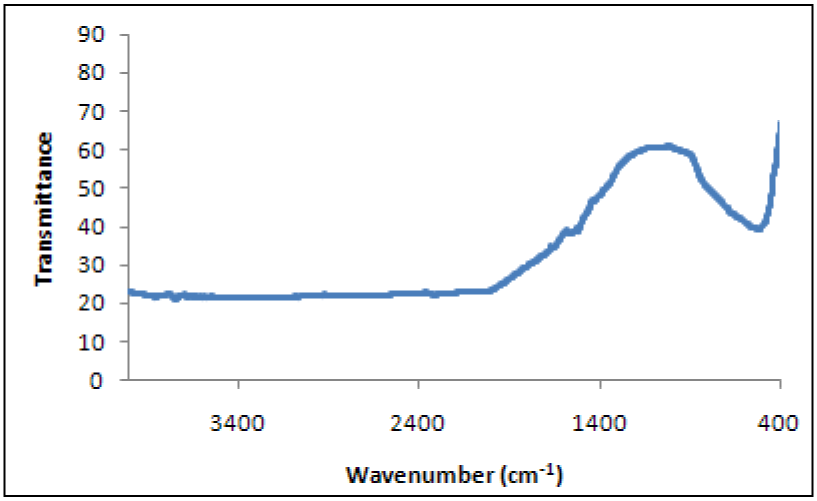

Fig. 3 FT-IR spectra of Cr-doped TiO_2 Photocatalyst

3.4. Result of SEM

The surface morphological study of the TiO_2 Photocatalyst was carried out using SEM image. Fig.4. shows the SEM image of the Cr-doped TiO_2 nanoparticles. It can be seen that the size of the TiO_2 is in the range of nanometer.

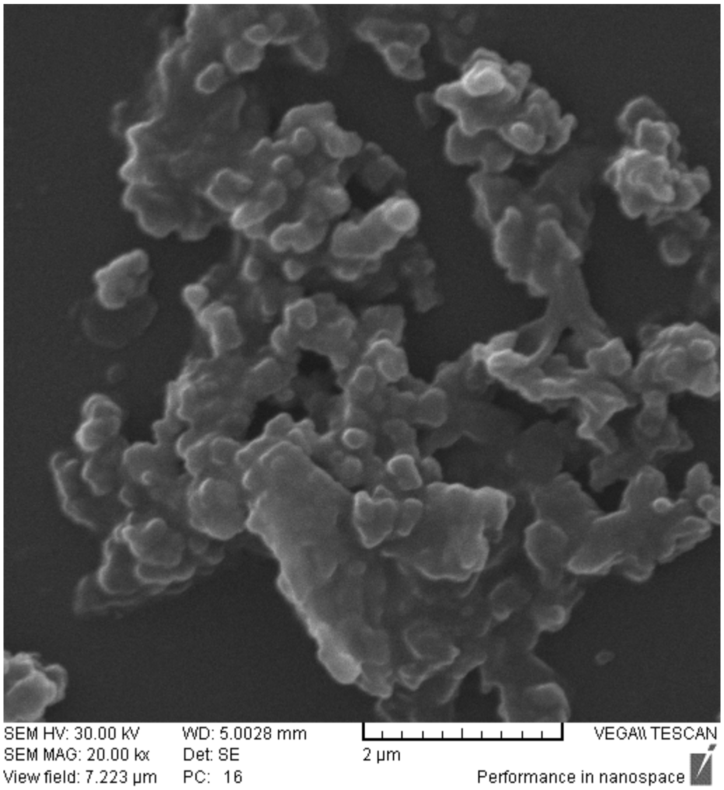

Fig. 4 SEM image of Cr-doped TiO$_2$ Photocatalyst

3.5. Photocatalytic activity

The Photocatalytic activitie for degradation of rhodamine B was investigated in water under visible light using prepared Cr-codoped TiO$_2$ (Fig. 5). As shown in Fig. 6, the photodegradation efficiency of rhodamine B was 98%, after 90 min.

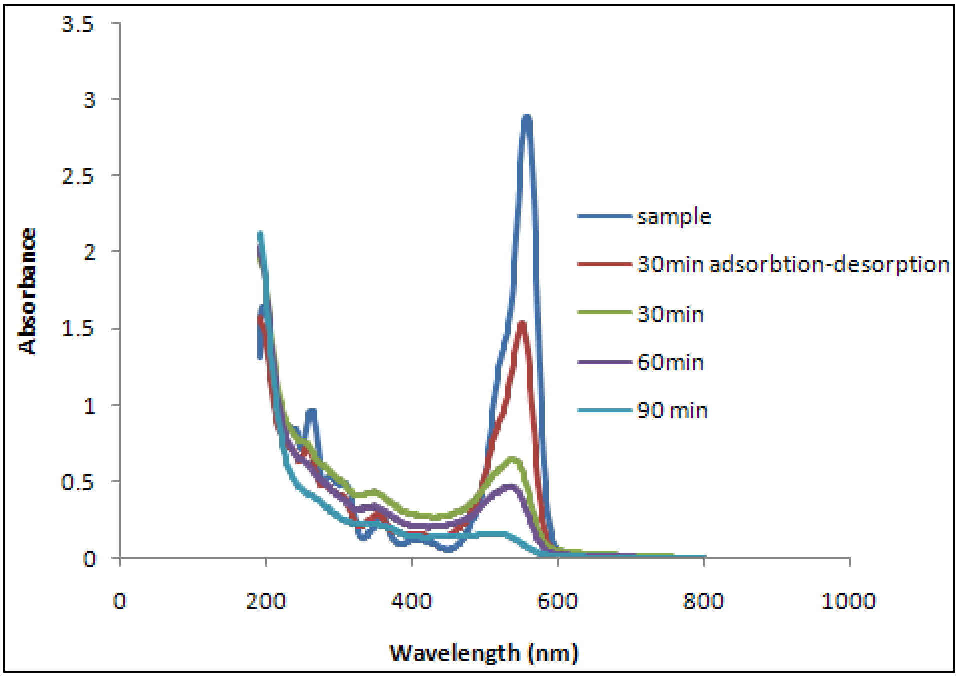

Fig. 5 The UV–vis absorption spectra of rhodamine B solution using Cr-doped TiO_2 after photodegradation with visible light. Condition: 100 ml of rhodamine B (10 ppm), 0.02 g catalyst, 90 min.

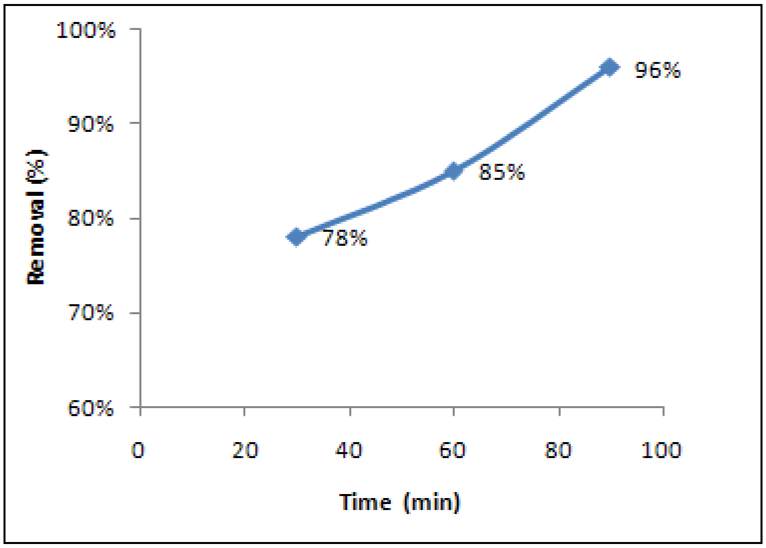

Fig. 6 Removal efficiency of photodegradation of rhodamine B

4. Conclusions

The mesoporous Cr-doped TiO_2 Photocatalyst with high activity for rhodamine B degradation under visible light was synthesized using SDS as a surfactant through a sol-gel method. The prepared photocatalysts were characterized by X-ray powder diffraction, IR spectra, SEM, UV-Visible absorption spectra. The XRD patterns shows anatase and phases. The obtained data from UV-Visible absorption spectra indicated that through the process of doping Cr with TiO_2, the wave length of TiO_2 absorption is increased (red shift). The Photocatalytic activitie for degradation efficiency of rhodamine B was 98%, after 90 min using prepared Cr-codoped TiO_2 in water under visible light.

Acknowledgements

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REFERENCES

[1] J.Sabate,M.Anderson,Kikkawa, J of catalysis, 127 (1991) 167-177
[2] Ning Ma,Xie Qua,Yaobin zhang, J of Membrane science, 335 (2009) 58-67
[3] Y.E. Benkli, M.F. Can, M. Turan, M.S. Celik, Water Res. 39 (2005) 487–493.
[4] N. Daneshvar, H. Ashassi Sorkhabi, M.B. Kasiri, J. Hazard. Mater. 112 (2004) 55–62.
[5] N. Takahashi, T. Nakai, Y. Satoh, Y. Katoh, Water Res. 28 (1994) 1563–1570.
[6] A. Mills, S.L. Hunte, J. Photochem. Photobiol. A 108 (1997) 1–35.
[7] D.A. Tryk, A. Fujishima, K. Honda, Electrochim. Acta 45 (2000) 2363–2376.
[8] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69–96.
[9] Z. Zou, J. Ye, K. Sayama, H. Arakawa, Nature 414 (2001) 625–627.
[10] A. Hagfeldt, M. Gr¨atzel, Acc. Chem. Res. 33 (2000) 269–277.
[11] T. Kawahara,Y.Konishi, H. Tada, N. Tohge, J. Nishii, S. Ito, Angew. Chem. Int. Ed. 41 (2002) 2811–2813.
[12] B. Ohtani, Y. Ogawa, S. Nishimoto, J. Phys. Chem. B 101 (1997) 3746–3752.
[13] N. Serpone, A.V. Emeline, Res. Chem. Intermed. 31 (2005) 391–432.
[14] S. Karvinen, Solid State Sci. 5 (2003) 811–819.

[15] A.D. Paola, E. Garc´ıa-L´opez, S. Ikeda, G. Marc‘ı, B. Ohtani, L. Palmisano, Catal. Today 75 (2002) 87–93.

[16] F. Cracia, J.P. Holgado, A. Caballero, A.R. Gonzalez-Elipe, J. Phys. Chem. B 108 (2004) 17466–17476.

[17] J. Zhu, Z. Deng, F. Chen, J. Zhang, H. Chen, M. Anpo, J. Huang, L. Zhang, Appl. Catal. B: Environ. 62 (2006) 329–335.

[18] J.B. Yin, X.P. Zhao, J. Phys. Chem. B 110 (2006) 12916–12925.

[19] J.C. Yu, G.S. Li, X.C. Wang, X.L. Hu, C.W. Leung, Z.D. Zhang, Chem. Commun. 25 (2006) 2717–2719.