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Enhanced photocatalytic activity for the degradation of rhodamine B by TiO_2 modified with Gd_2O_3 calcined at high temperature

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ABSTRACT

TiO_2 modified with Gd_2O_3 (Gd/TiO_2) nanoparticles were prepared by an impregnation method using TiO_2-500 °C support (anantase phase) or TiO_2-650 °C support (mixed phases of anatase and rutile), respectively. The surface and bulk crystalline phases of Gd/TiO_2 have been characterized by UV Raman spectroscopy and XRD. Besides, the morphology, particle size, and the optical properties of Gd/TiO_2 have been studied by TEM, BET, and UV–visible diffuse reflectance spectra. It is interesting to note that the surface crystalline phase (surface anatase phase or surface mixed phases) of TiO_2 which has been impregnated with Gd_2O_3 can be stabilized after calcination at 800 °C. This work provides a promising method for controlling the surface phase, crystallinity, and particle size of TiO_2 at high temperatures. Moreover, photocatalytic activity of Gd/TiO_2 has been evaluated by degradation of rhodamine B and 4-chlorophenol in aqueous solution under UV irradiation. It is found that Gd/TiO_2 exhibits good photocatalytic activity compared to pure TiO_2. The higher photocatalytic activity of Gd/TiO_2 is mainly attributed to an increase in the anatase crystallinity, an increase in photoinduced charge separation, which induced by surface phase junction, and to an increase in the extent of its optical absorption spectrum, as compared to TiO_2.

1. Introduction

Heterogeneous photocatalysis by semiconductors has been shown to be a promising method in photocatalytic decomposition of various organic compounds in wastewater treatment, environment purification, and solar energy conversion [1–7]. Compared to other semiconductor photocatalysts, titania (TiO_2) has turned out to be the semiconductor with the highest photocatalytic activity, being non-toxic, stable in aqueous solution and relatively inexpensive [8,9]. The catalytic performance of TiO_2 is a function of many factors, mainly phase structure, specific surface area, crystallite size, particle shape, and surface hydroxyls. The crystal structure and the composition of TiO_2 can significantly affect its photocatalytic activity [10–12]. Anatase and rutile are TiO_2 polymorphic forms which are relevant in photocatalytic applications.

As is well known, sol–gel [13], precipitation methods [14] and many physical and chemical approaches [15–17] have succeeded to synthesize anatase and rutile TiO_2 catalysts. In these methods, high temperature ca.>450 °C calcination is usually required to form regular crystal structure. However, the high temperature treatment has some detrimental effects on the photocatalytic activity of TiO_2. For instance, it declines the surface area and reduces the surface hydroxyl groups of TiO_2 on one hand. On the other hand, rutile phase with hard agglomeration and large particle size appears in TiO_2 easily after high temperature treatment. Thus, a question requires to be addressed: how can we keep the high photocatalytic activity of TiO_2 after calcination especially after calcination at high temperature calcination?

In our previous research [18], it was found that the optimized photocatalytic activity of TiO_2 can be obtained from a mixture of the two phases, which was ascribed to the formation of a surface-phase junction between anatase and rutile. The contact between anatase and rutile is beneficial for the charge separation. Thus, surface-phase junction has provided guidance in the photocatalyst preparation.

Various methods have been employed to control the crystal phases of TiO_2. Doping with other elements, such as rare metals and non-metals, has been widely used for TiO_2 modification to increase the anatase thermal stability and reduce the agglomeration of TiO_2 therefore improve its photocatalytic activity [19–23]. Besides, incorporation of lanthanide ion into TiO_2 also enhance the photocatalytic performance of TiO_2 [24–28] has been enhanced

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by increasing the photocurrent response and the separation of electron–hole pairs under UV illumination. Xu et al. [29] present a comparative study on the photocatalytic efficiency of bareTiO_2 and RE-doped titania (RE = La^{3+}, Ce^{3+}, Er^{3+}, Pr^{3+}, Gd^{3+}, Nd^{3+}, Sm^{3+}) prepared by the sol–gel method. It is found that Gd^{3+}-doped TiO_2 shows the highest activity among all RE-doped samples investigated because of the increase in the interfacial electron transfer rate.

Until now, most results mainly focused on the correlation of the properties and amounts of lanthanide ion and bulk phase of TiO_2. We are interested in precise control the surface phase of TiO_2 calcined at high temperature by lanthanide ion. This paper attempts to control the surface phase of TiO_2 by Gd_2O_3, and we preferred to control the surface phase of TiO_2 calcined at high temperature at the mixed phase because the anatase–rutile mixed phases are benefit for separation of electron and holes.

In this work, we studied Gd_2O_3 surface modified TiO_2 samples (Gd/TiO_2) prepared by impregnation method using UV Raman spectroscopy, XRD, UV–visible diffuse reflectance spectroscopy (UV–vis DRS), BET, and TEM. The photocatalytic activity tests show that upon calcination at high temperature the Gd/TiO_2 exhibits higher photocatalytic activity than pure TiO_2. It can be concluded that the higher photocatalytic activity of Gd/TiO_2 is mainly attributed to an increase in the anatase crystallinity, an increase in photoinduced charge separation, which induced by surface phase junction, and to an increase in the extent of its optical absorption spectrum, as compared to TiO_2.

2. Materials and methods

2.1. Synthesis of Gd_2O_3 surface modified TiO_2

Gd_2O_3 surface modified TiO_2 (Gd/TiO_2) was prepared by a wet impregnation method. TiO_2 was synthesized by the hydrolysis of titanium (IV) *n*-butoxide ($Ti(OBu)_4$) as reported in our previous work [30]. Required amount of $Ti(OBu)_4$ in anhydrous ethanol was taken (1:2 ratio by volume). An ammonia solution was added to the mixture drop by drop under constant stirring until the pH of the solution reached 9. The resulting white precipitate was stirred for 24 h, it was then washed twice with deionized water and anhydrous ethanol and subsequently dried at 100 °C for 12 h to obtain amorphous TiO_2.

The as-prepared amorphous TiO_2 was calcined at 500 °C(TiO_2-500 °C) and 650 °C (TiO_2-650 °C) prior to the usage as a support for Gd/TiO_2(500 °C) and Gd/TiO_2(650 °C), respectively. The support was impregnated with aqueous solution of various concentrations of gadolinium nitrate ($Gd(NO_3)_3{\cdot}6H_2O$), and subsequently stirred in a hot water bath until it was dried. After the sample was kept at 110 °C overnight, it was calcined at different temperatures in air for 3 h. After calcination, the TiO_2 and Gd/TiO_2 samples are denoted as TiO_2-T and nGd/TiO_2-T, where n represents the amount of Gd_2O_3 (wt.%) and T represents the calcination temperature, respectively.

2.2. Catalyst characterization

The bulk crystalline phase of TiO_2 and Gd/TiO_2 was characterized by XRD, while UV Raman spectroscopy was used to characterize their surface crystalline phases. X-ray powder diffraction (XRD) patterns were obtained on a Rigaku MiniFlex diffractometer with Cu Kα radiation source. The weight fraction of the rutile phase in the TiO_2 sample, W_R, can be estimated from the XRD peak intensities using following formula [31]:

$$W_R = \frac{1}{[1 + 0.884(A_{ana}/A_{rut})]},$$

where A_{ana} and A_{rut} represent the X-ray integrated intensities of anatase (1 0 1) and rutile (1 1 0) diffraction peaks, respectively. UV Raman spectra were measured at room temperature with Jobin-Yvon T64000 triple-stage spectrograph with spectral resolution of 2 cm^{-1}. The laser line at 325 nm of a He–Cd laser was used as an exciting source with an output of 25 mw. The surface phase compositions of TiO_2 and Gd/TiO_2 samples are estimated from the UV Raman spectra according to our previous work [30]. Transmission electron microscopy (TEM) was taken on a JEOL 2000EX for estimating particle size and morphology. Ultraviolet–visible diffuse reflectance spectra were recorded on a JASCO V-550 UV–vis spectrophotometer. The Brunauer–Emmett–Teller (BET) surface areas of TiO_2 and Nd-TiO_2 samples were measured by nitrogen adsorption at 77 K using a Micromeritics ASAP 2000 adsorption analyzer.

2.3. Photocatalytic experiment

The detailed process was as following: 50 mg of TiO_2 sample (or Gd/TiO_2 sample) was added into 60 ml of 20 mg/L RhB solution (or 60 ml of 20 mg/L 4-chlorophenol solution). The suspension was stirred in dark for 30 min to obtain adsorption–desorption equilibrium of dye before illumination. A 250 W high voltage mercury lamp (λ = 365 nm, Shanghai Yaming Lighting Co.) was used as light source. At a defined time interval, 3 ml suspension was removed and immediately centrifuged. Then, the concentration of RhB (or 4-chlorophenol) was analyzed using the UV–vis spectrophotometer (UV-1102 spectrophotometer, Shanghai Tianmei technology Co., Ltd.).

3. Results and discussion

3.1. XRD and UV Raman analysis of 3Gd/TiO_2(500 °C) calcined at different temperatures

Fig. 1 shows the XRD patterns of 3Gd/TiO_2(500 °C) samples calcined at various temperatures between 600 and 800 °C. Five distinctive TiO_2 peaks at 25.4, 37.9, 48.1, 53.8, and 55.0°, corresponding to anatase (1 0 1), (0 0 4), (2 0 0), (1 0 5), and (2 1 1) crystal planes [32] are observed for TiO_2-500 °C, suggesting that TiO_2-500 °C support is in the anatase structure. For TiO_2-800 °C, only characteristic peaks due to rutile phase are observed at 2θ = 27.6, 36.1, 41.2 and 54.3° [32], which indicate that TiO_2-800 °C is in the rutile phase.

The 3Gd/TiO_2(500 °C) samples calcined at different temperatures have significant diffraction peaks representing the characteristic of anatase phase. Compared with un-modified TiO_2, the 3Gd/TiO_2(500 °C) exhibits high anatase thermal stability, which means that the anatase-to-rutile phase transformation was effectively inhibited by 3 wt.% Gd_2O_3. Moreover, Fig. 1 displays that, the intensity of diffraction peaks of anatase TiO_2 increased when the calcination temperature was increased from 600 to 800 °C. Enhancement of the intensity is attributed to increase of the anatase crystallinity of the 3Gd/TiO_2(500 °C) samples as a result of the calcination temperature is increased from 600 to 800 °C.

From XRD patterns, the crystallite sizes of these samples are calculated by Scherrer formula:

$$D = \frac{k\lambda}{\beta \cos\theta},$$

where D is the crystalline size, k the constant usually taken as 0.89, λ the wavelength of X-ray radiation (0.1541 nm), β is the peak width at half-maximum height after subtraction of equipment broadening, and θ is the diffraction angle. The crystallite sizes of the 3Gd/TiO_2(500 °C) samples are shown in Table 1. Compared with the particle size of TiO_2-800 °C and 3Gd/TiO_2(500 °C)-800 °C, it is obvious that Gd^{3+} inhibits the particles growth of TiO_2, even at the