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Synthesis of Sc and V-doped TiO_2 nanoparticles and photodegradation of rhodamine-B

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ABSTRACT

Anatase TiO_2 nanoparticles doped with Sc and V were synthesized and their photocatalytic activities were evaluated through the photodegradation of rhodamine-B under UV irradiation. TiO_2 shows the highest photocatalytic activity and Sc doped TiO_2 and V doped TiO_2 show lower photocatalytic activity than TiO_2. In contrast, Sc and V codoped TiO_2 shows no any photocatalytic activity. The reasons for the decrease in photocatalytic activity is due to the presence of surficial Sc_2O_3 islands covering the reactive sites for Sc doped TiO_2 and the increased e−/h+ pair recombination resulted from the high level substitutional V(IV) ions for V doped TiO_2, respectively.

1. Introduction

TiO_2 has been intensively investigated for many years because of its applications in many fields, such as photocatalysis [1,2], sensors [3,4], solar cells [5,6] and electronic-ink [7,8]. The properties of TiO_2 are determined by its phase, surface states, dopant, doping level, crystallization degree, size and morphology. For TiO_2 photocatalysis, the main efforts have been made in two aspects: One is to narrow the wide bandgap to extend the spectral response of TiO_2 to the visible region for the efficient utilization of the energy from the sun and some attempts has been tried by doping nonmetallic dopant to narrow the bandgap of TiO_2, e.g., nitrogen [9,10], carbon [11,12] and sulfur [13,14]. Another is to reduce the recombination rate of photogenerated electron-hole pairs by doping metal dopant to enhance efficiency of photolysis. In general, it has been accepted that the presence of metal dopant in the TiO_2 crystalline matrix significantly influences photoreactivity, charge carrier recombination rates, and interfacial electron-transfer rates. The concentration of metal dopant plays a very important role in photocatalytic activity. At low concentration, the photocatalytic activity increases with doping concentration, at which metal dopant act as trapping centers for photo-generated electron (e−) and/or hole (h+) within TiO_2, and reaches the maximum at optimal concentration, and then decreases with doping concentration due to the increased e−/h+ pair recombination rate.

The optimal concentration is related to the kind of dopant. Various dopants with mostly doping level ranging from 0.1 to 1.0 at.% have been used to investigate their effect on the photocatalytic activity [15]. Some attempts have also been tried to evaluate the dependence of photocatalytic activity on doping level [16]. Codoping with metallic and/or nonmetallic dopants has also been used to investigate their synergetic effect for the enhancement of performance of TiO_2 [17–20]. It was reported that doping with trivalent or pentavalent metal ions was detrimental to the photocatalytic reactivity [21] while doping with cations of valency higher than that of Ti^{4+} enhanced photoreactivity [22]. Vanadium (V) is often chosen as a dopant while scandium (Sc) was seldom used as the dopant for TiO_2 [23].

In this study, 2.0 at.% Sc and 2.0 at.% V codoped, single doped and undoped TiO_2 nanoparticles were synthesizied by sol–gel method and calcined at 500 °C for 6 h and their photocatalytic activities were investigated through the photodegradation of rhodamine-B (RhB) under UV light irradiation. The purpose of this study is to observe the influence of Sc and V dopants on the photocatalytic activity of TiO_2 and explain the possible reason for the obtained results.

2. Experimental

2.1. Sample preparation

All chemicals were obtained from Aldrich Chemical Co. and used as received. The cheap scandium oxide (Sc_2O_3, 99.9%) and vanadium pentoxide (V_2O_5, 99.6%), which both can be dissolved in

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concentrated acid, were used as Sc and V sources instead of expensive scandium, chloride($ScCl_3$) and vanadium tetrachloride(VCl_4). For the synthesis of 2.0 at.% Sc doped TiO_2, after addition of 38 mg (0.28 mmol) of Sc_2O_3 to 200 mL of deionized water, 3 mL (27 mmol) of titanium tetrachloride ($TiCl_4$, 99.9%) was dropwise added to the solution under heavy stirring at room temperature. Hydrolysis of $TiCl_4$ occurred immediately, as indicated by the appearance of turbidity. After stirring for 2 h, 7.3 mL of ammonia solution (28%) was dropwise added to the solution to complete formation of TiO_2. During the period of stirring, Sc_2O_3 was considered to be completely dissolved by the hydrochloride produced by hydrolysis of $TiCl_4$ [24]. After another stirring for 1 h, 2.0 at.% Sc doped TiO_2 nanoparticle was gathered and washed 3 times with deionized water by centrifugation to remove the hydrochloride and ammonia residual in the product. The final product was dried in a oven at 60 °C over night. The synthetic processes for pure TiO_2, V doped TiO_2, and Sc and V codoped TiO_2 are the same as the above procedure. For the synthesis of 2.0 at.% V doped TiO_2, 51 mg (0.28 mmol) of V_2O_5 was used as V source. For the synthesis of 2.0 at.% (Sc + V) codoped TiO_2, 38 mg (0.28 mmol) of Sc_2O_3 and 51 mg (0.28 mmol) of V_2O_5 were used as Sc and V sources. All the as-synthesized products were almost amorphous phase and calcined at 500 °C for 6 h to obtain crystalline TiO_2. For the simplicity, Sc doped TiO_2, V doped TiO_2, and Sc and V codoped TiO_2 samples are denoted as TiO_2-Sc, TiO_2-V and TiO_2-Sc-V, respectively.

2.2. *Characterization*

X-ray powder diffraction (XRD) measurements were carried out using a diffractometer (Rigaku, D/MAX-3C) with Cu K_α radiation source (λ = 0.154056 nm) to determine the crystalline phase and estimate crystallite size of the samples. The morphologies and particle sizes of the samples were observed by transmission electron microscopy (TEM) on a JEOL JEM-1200EX.

2.3. *Photocatalytic activity measurements*

The photocatalytic activity of the four samples was evaluated through the photodegradation of RhB under UV light irradiation. A 30 W UV lamp (253.7 nm, Beijing Yuquan Xingguang Electric Equipment Limited Company) was used as the light source. In a typical photocatalytic reaction, 20 mg of photocatalyst was added into 50 mL deionized water and sonicated for 1 h to well disperse the photocatalyst in the water, and then 0.5 mg of RhB was added into the solution. Prior to the irradiation, the solution was stirred for 30 min in the dark to reach adsorption/desorption equilibrium, and then the solution was exposed to UV light while being continuously stirred. At intervals of 1 h, 2 mL sample was taken from the solution and immediately centrifuged to remove the photocatalysts. The collected supernatant was then scanned from 700 nm to 200 nm using a UV–vis spectrophotometer (HITACHI, U-3010) to obtain the corresponding UV–vis absorption spectra of RhB. After UV–vis spectrum measurement each time, both the removed photocatalysts and supernatant were put back into the solution to keep the identical condition.

3. Results and discussion

Fig. 1(c)–(f) shows the XRD patterns of TiO_2, TiO_2-Sc, TiO_2-V and TiO_2-Sc-V, respectively, and Fig. 1(a) and (b) shows the XRD patterns of Sc_2O_3 and V_2O_5 for reference, respectively. It is clear that all the four samples can be indexed to the anatase phase of TiO_2 (PDF no. 21-1272) with some brookite phase (PDF no. 29-1360, indicated by symbol B) for TiO_2 and TiO_2-Sc, respectively. No any characteristic peaks from Sc_2O_3 and V_2O_5 are found in the XRD patterns for the doped samples, implying that Sc and V dopants are well dispersed in the TiO_2 matrix or Sc and V oxides are so small in content that they cannot be detected by XRD technique. Similar result was obtained in our previous work [23].

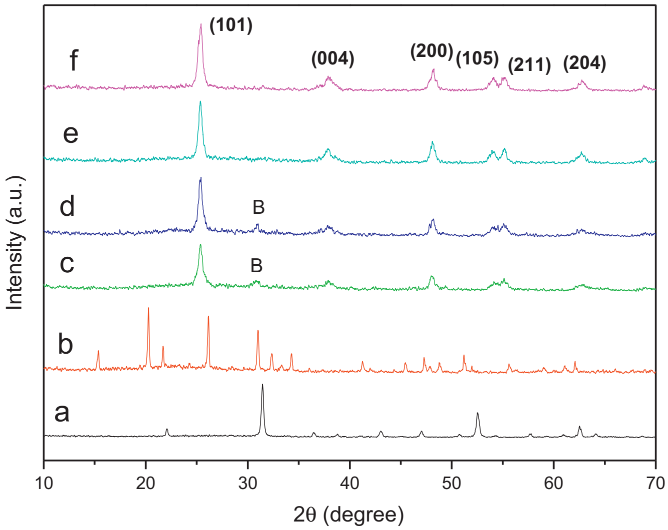

Fig. 1. XRD patterns: (a) Sc_2O_3, (b) V_2O_5, (c) TiO_2, (d) TiO_2-Sc, (e) TiO_2-V, and (f) TiO_2-Sc-V. Symbol B indicates the brookite phase.

It is well known that sol-gel synthesis of TiO_2 generally produces a mixture of brookite and anatase [25,26]. Using $I_{B(1\,2\,1)}/(I_{B(1\,2\,0)}+I_{A(1\,0\,1)})$ [27], where $I_{B(1\,2\,1)}$ and $I_{B(1\,2\,0)}$ are the intensity of (1 2 1) and (1 2 0) diffraction peaks of brookite, respectively, and $I_{A(1\,0\,1)}$ is the intensity of (1 0 1) diffraction peak of anatase, the brookite content is estimated to be 13.9 wt% and 17.2 wt% for TiO_2 and TiO_2-Sc, respectively. Here, the overall intensity at ~25.3° is used as $I_{B(1\,2\,0)}+I_{A(1\,0\,1)}$ because of superposition of (1 2 0) diffraction peak of brookite with (1 0 1) diffraction peak of anatase. The results are consistent with the report [25], which showed that brookite content increased with increasing Ti/H_2O ratio and pH value.

The formation of brookite is explained as the following: With dropwise addition of the $TiCl_4$ starting material into water, the reaction solution became strongly acidic and some specific complexes, $Ti(OH)_4$ (maximum above pH = 5), $Ti(OH)_3^+$(maximum at pH = 3), and $Ti(OH)_2^{2+}$ (maximum below pH = 1), which are considered to be responsible for the nucleation of TiO_2 as a intermediate, were in turn formed with decrease of pH value during the stirring of 2 h [28]. The reaction solution showed semitransparent with light white probably due to the nucleation of anatase and brookite. It is considered that in the sol–gel process, the amount of water determines the degree of hydrolysis and the type of initial species formed [28] and the increased water content results in an increased anatase-to-brookite ratio [25]. The probability for the formation of the specific polymorph was reported to be proportional to the number and type of growth units [26]. The growth units have been confirmed to be the short range order unit similar to that in anatase and brookite [26]. The growth units should be resulted from the nucleation of anatase and brookite. Anatase with ~25% brookite was obtained at ca. pH = 1 [28]. Therefore, we suggest that after the stirring of 2 h, ~75% anatase growth units, ~25% brookite growth units and major $Ti(OH)_2^{2+}$ species with minor $Ti(OH)_3^+$ species were formed in the strongly acidic reaction solution [28]. The $Ti(OH)_3^+$ species was considered as the precursor complex to anatase in the gel–sol system [28]. And then, with dropwise addition of the NH_3 solution into the reaction solution and another stirring of 1 h, $Ti(OH)_3^+$ and $Ti(OH)_4$ species increased in turn gradually with the increase of pH