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Preparation of vanadium-doped titanium dioxide neutral sol and its photocatalytic applications under UV light irradiation

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ABSTRACT

A sol–gel method was used to prepare V-doped TiO_2 sol. $TiCl_4$ was converted to $Ti(OH)_4$ and H_2O_2 was then added to convert it to TiO_2 at high temperature. The sols with various contents of V were used to prepared thin films on glass substrate by dip-coating method. The as-prepared samples were characterized by X-ray diffraction, scanning electron microscope, transmission electron microscope, high resolution transmission electron microscope (HRTEM), X-ray photoelectron spectroscopy, and UV–vis spectroscopy. The photocatalytic activities of the V-TiO2 thin films were investigated by the degradation of methylene blue under UV light irradiation. The as-prepared V-TiO_2 sol was neutral and showed high stability of nanoparticles suspended in the sol without any surfactant. The shape of particle was rhombus and possessed high aspect ratio. The V-TiO_2 particles were in anatase and nanosize, so they do not need annealing process to form crystals after coating on the substrate. V doping can produce more photogenerated electrons and holes, which improved the photocatalytic activity. However, overdoes V in TiO_2 would lead to form the recombination centers and suppressed the activity. The optimum NH_4VO_3/TiO_2 weight ratio in starting materials was 3%.

1. Introduction

Heterogeneous photocatalysts have been applied extensively on self-cleaning [1–3], water and air purification [4,5], anti-fogging [6,7], anti-corrosion [8–12], and antibacterial [13]. TiO_2 is the most widely studied photocatalytic material because of its strong oxidizing abilities, stability, nontoxicity, and low cost. However, TiO_2 displays its photoactivity only under ultraviolet (UV) light irradiation with its wide band-gap of TiO_2 (3.2 eV) which means that it can be stimulated only by the wavelength below 388 nm. As a result, only about 3–5% of solar energy on the earth's surface can be utilized and is therefore limit the practical applications [14]. Sasirekha et al. [15] reported a sol–gel method to synthesize the suspension neutral TiO_2 sol without adding surfactant by using $TiCl_4$ as a precursor and H_2O_2 as an oxidizing agent. The as-prepared sols with nanosized particles could be easier to apply on various kinds of substrates. Liu et al. [16] dried the as-prepared sols to obtained V-doped TiO_2 powders, which had problems related to separation and aggregation. Since TiO_2 powder has problems of separation and aggregation and is difficult to recycle, it cannot be used in industrial waste water treatment. Thin film photocatalyst deposited on appropriate substrate can be easily recovered and reused.

In this study, we aimed to develop a synthesis method of V-doped TiO_2 hydrosols with different compositions, which is neutral, easily coats on glass, and possess high photocatalytic activity. In this study, vanadium precursor (NH_4VO_3) was added into TiO_2 sol during the preparation process to obtain V-TiO_2 sol which was further coated on glass substrate by dip-coating method.

2. Experimental

2.1. Materials

Titanium tetrachloride was purchased from Showa. NH_4OH was purchased from Showa. Ammonium metavanadate was purchased from Merck Chemicals. Distilled water was used throughout the experiments. Methylene blue was purchased from Alfa Aesar.

2.2. Synthesis of V-doped TiO_2 sols

V-doped TiO_2 sols were prepared by the sol–gel method. The procedure of preparing TiO_2 and V-doped TiO_2 sols was as follows. Titanium tetrachloride ($TiCl_4$) was slowly added dropwise into 150 mL 1 M HCl aqueous solution under magnetic stirring, and kept in ice

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bath to maintain the temperature at 0 °C for 30 min. Aqueous solution of 1 M NH_4OH was then added slowly to the solution to adjust the pH value to ~8.0 to form white hydrated titanium oxide gel, $Ti(OH)_4$. After aging and stirring for a period of time, $Ti(OH)_4$ gel was washed with distilled water several times until no chloride ion in the solution. The gel was then filtered and dried at room temperature. $Ti(OH)_4$ gel was repulped in distilled water under magnetic stirring for 1 h to form a milky solution. An aqueous solution of hydrogen peroxide (30 wt% H_2O_2) was added to the solution under stirring for 1 h. NH_4VO_3 was added at the same time. This solution was heated at 95 °C for 12 h under magnetic stirring and a light yellow transparent V-TiO_2 sol was obtained. The preparation conditions of this study were as follows: the mole ratio of H_2O_2:TiO_2 was 6:1 and the weight ratio of NH_4VO_3:TiO_2 was 1:100, 2:100, 3:100, and 4:100, which denoted as VT1, VT2, VT3, and VT4, respectively.

2.3. Preparation of V-doped TiO_2 films

V-TiO_2 thin film was coated on soda lime glass substrate by dip-coating. The glass substrate was cleaned by NaOH solution with ultrasonic for 1 h, finally rinsed with ethanol and dried in an oven at 50 °C. The glass substrate was vertically dipped into the as-prepared sol with the withdrawal speed of 60 cm/min for 10 times. TiO_2 and V-doped TiO_2 films were denoted as *T* and VT(*X*), where *X* is the weight ratio of NH_4VO_3:TiO_2. The total coating surface area of each glass substrate was 35 cm^2.

2.4. Characterization

XRD was carried out on a Siemens D500 powder diffractometer using Cu K_α radiation (1.5405 Å) at a voltage and current of 40 kV and 40 mA, respectively. The canning range was $2\theta = 20$–$80°$ at a rate of 0.05°/min.

The morphology and the thickness of the V-TiO_2 films were observed by SEM. SEM images were obtained by Hitachi HI–3000 with a tungsten lamp using an acceleration voltage of 15 kV and emission current of 81,000 nA. Before the SEM analysis, the samples were coated with platinum to increase their conductivity. SEM images were recorded at magnification of 100,000× and 150,000×.

The morphology and structure of the sample were investigated by TEM on JEM–2000 EX II operated at 160 kV and HRTEM on a JEOL JEM–2010 operated at 200 kV. The suspended V-TiO_2 particles were deposited on the holey carbon-coated copper grid (300#) (Ted Pella).

The surface compositions and chemical states of the samples were determined by XPS with a Thermo VG Scientific Sigma Prob spectrometer. The XPS spectra were collected using Al K_α radiation at a voltage and current of 20 kV and 30 mA, respectively. The base pressure in the analyzing chamber was maintained in the order of 10^{-7} Pa. The pass energy was 23.5 eV and the binding energy was calibrated by contaminant carbon (C 1s = 284.5 eV). The peak fitting of each spectrum was carried out by using XPSPEAK software with Shirley type background and 30:70 Lorentzian/Gaussian peak shape were adopted to deconvolute the peak.

The optical absorption spectra measurement was investigated by using UV–vis spectrophotometer (Varian Cary Bio 300) in the range of 200–800 nm.

2.5. Photocatalytic activity

In the photocatalytic activity test, 100 ml of methylene blue (MB) aqueous solution with the concentration of 10 mg/L was loaded in a quartz cell. The glass slide coated V-TiO_2 film was dipped into the MB solution vertically. Before the photocatalytic activity test, the reactor was kept in dark under magnetic stirring for 30 min for saturation adsorption of MB. The reaction was carried out in a cylindrical container by top scattering of UV light. The UV light source was a 20 W UVC lamp (wavelength = 254 nm). The lamp to the surface of the solution was 10 cm, and the concentration of MB aqueous solution was determined every 2 h interval for 12 h by a UV–vis spectrophotometer (Varian Cary Bio 300). The concentration of MB was determined by the intensity of the peak at wavelength of 664 nm, which is the highest characterized adsorption wavelength of MB.

Table 1
pH value of the as-prepared sols.

As-prepared sols	Wt. ratio of NH_4VO_3:TiO_2	pH value
TiO_2	0:100	7.07
VT1	1:100	7.72
VT2	2:100	7.54
VT3	3:100	7.57
VT4	4:100	7.70

3. Results and discussion

3.1. Characteristics of TiO_2 and V-TiO_2 sols

The as-prepared TiO_2 and V-TiO_2 sol were stable suspension without adding surfactant. The color of the sol was more yellowish as the V concentration increased. The pH values of TiO_2 sol and V-TiO_2 sol are listed in Table 1. The as-prepared sols are neutral with pH values at about 7–8. These neutral sols could be coated on any kind of substrate without corrosion. Furthermore, it does not need to anneal at high temperature to obtain anatase structure because the V-TiO_2 particles dispersed in sols were in anatase phase as shown in latter section.

3.1.1. HRTEM images

Morphologies of the as-prepared samples were investigated by HRTEM. Fig. 1 shows the HRTEM photos of pure TiO_2 and V-doped TiO_2 particles in sols. It can be seen that the morphology of pure TiO_2 is rhombus shape with the long-axis of 20–40 nm, and the short-axis of 5–10 nm. V-doped TiO_2 particles exhibit irregular spherical shape with particle size ranging from 10 to 30 nm, and no vanadium oxide compounds were detected as confirmed by SAED. This confirms that V ions were incorporated into TiO_2 lattice. The HRTEM pattern as illustrated in Fig. 2 of lattice space of 0.347 nm is consistent with (1 0 1) plane of anatase TiO_2.

3.1.2. XRD

The as-prepared sols were dried at 60 °C for several days to obtain the powder samples. Their XRD patterns are shown in Fig. 3. The diffraction peaks at $2\theta = 25.3°, 37.7°, 48.1°, 53.8°$, and $62.7°$ of all the samples are indexed to (1 0 1), (0 0 4), (2 0 0), (1 0 5) and (2 0 4) planes of anatase of TiO_2 (JCPDS card 78-2486). No anatase-to-rutile phase transformation was observed [17–19]. In addition, no characteristic peak of vanadium oxide (V_2O_5 and V_2O_4) was detected, indicating that there was no vanadium oxide phase precipitated on TiO_2 surface after heat treatment, implying that V oxides were highly dispersed with very small particles (≦4 nm). The average crystallite size was calculated by using the Debye–Scherer equation, and the results are listed in Table 2.

Table 2
Crystallite size of TiO_2 and V-doped TiO_2.

Catalyst	Crystallite size (nm)
TiO_2	11.62
VT1	10.85
VT2	11.62
VT3	7.75
VT4	5.81