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Solar photocatalytic activities of porous Nb-doped TiO_2 microspheres by coupling with tungsten oxide

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ABSTRACT

Nb doped TiO_2 microspheres modified with WO_3 (Nb-TiO_2/WO_3) was prepared by ultrasonic spray pyrolysis method combined with impregnation method. The microspheres were characterized with SEM, TEM, XRD, BET, photoluminescence and UV–vis absorption spectra. The Nb-doping was observed to extend the spectral absorption of TiO_2 into visible spectrum, and the absorption onset was red-shifted for about 88 nm compared to pristine TiO_2 microspheres. Nb-TiO_2/WO_3 microspheres do not display a red-shifted absorption edge compared with Nb doped TiO_2 microspheres. Under solar irradiation, Nb-TiO_2/WO_3 microspheres showed higher photocatalytic activity for methylene blue degradation compared with that of pure TiO_2 microspheres and Nb doped TiO_2 microspheres, which could be ascribed to the extended light absorption range and the suppression of electron-hole pair recombination.

1. Introduction

Being an excellent photocatalyst, titanium dioxide (TiO_2) has been extensively investigated for more than three decades due to its excellent properties, such as non-toxicity, high thermal-stability and low cost [1–3]. However, extending band gap excitation of TiO_2 into the visible spectrum is still a critical issue for the development of solar light-driven photocatalysts. One of the most common method for reaching this goal is to narrow the band gap of TiO_2 by doping it with transition metal cations (e.g., Cr, V, Fe, and Ni) [4–7]. Nb-doped TiO_2 has rapidly raised interest in recent years for its promising applications in transparent conductive films, dye-sensitized solar cells, sensors [8–13] and photocatalyst material [14–16]. The ionic radius of Nb^{5+} is only a bit larger than Ti^{4+} $\left(r_{(\mathrm{Ti}^{4+})} = 0.605\,\text{Å}\ \text{versus}\ r_{(\mathrm{Nb}^{5+})} = 0.64\,\text{Å}\right)$. Therefore, Nb^{5+} can be easily doped into the lattice of TiO_2 at high concentration. Besides, Nb doping will introduce donor levels below the CB edge of TiO_2 [17–19]. The electronic transition from VB to these donor levels will be excited by the visible light and, therefore, render the Nb-doped TiO_2 photocatalyst to be visible light responsive, like what nonstoichiometric TiO_2 performs [20]. However, since electrons in the deep level can not efficiently reduce dioxygen, they will go another way to recombine with photogenerated holes, which is also detrimental to photocatalytic process. Thus, enhanced charge separation is necessary in Nb-doped TiO_2 system. TiO_2/WO_3 system has been applied in electrochromic devices [21], photochromic devices [22–26] and dye-sensitized solar cells [27]. WO_3 ($E_g \approx 2.8$ eV) has a suitable conduction band edge to form a type II heterojunction with TiO_2, which enables the transfer of photogenerated electrons from TiO_2 ($E_g \approx 3.2$ eV) to WO_3 and hole transfer in the opposite direction [28–30]. Therefore, TiO_2/WO_3 heterostructured materials have also been frequently investigated for photocatalytic degradation of organic pollutants [28,31–34]. Some groups reported enhanced photocatalytic activity of TiO_2/WO_3 for monocrotophos, acid red stearic acid and toluene [35–38].

In our previous work, we have prepared Nb-doped TiO_2 microspheres. The results showed that 5 mol% Nb-doped TiO_2 microspheres showed higher photocatalytic activity for methylene blue degradation compared with that of pure TiO_2 microspheres and 2 mol% Nb doped TiO_2 microspheres [39]. In addition, we have also prepared TiO_2/WO_3 porous microspheres. The results showed that TiO_2/WO_3 porous microspheres with W/Ti molar ratio of 2% showed the highest photocatalytic activity for acetaldehyde degradation [40]. It seems to be that low WO_3 content in TiO_2 show high photocatalytic activity. We assume Nb doped TiO_2 microspheres modified with WO_3 should show high photocatalytic activity due to the extended light absorption range and the suppression of electron–hole pair recombination.

In the present work, we prepared TiO_2 and Nb doped TiO_2 microspheres (Nb-TiO_2) by the ultrasonic spray pyrolysis (USP) method and Nb doped TiO_2 microspheres modified with WO_3

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($Nb-TiO_2/WO_3$) by ultrasonic spray pyrolysis method combined with impregnation method. The USP method is versatile for producing functional materials on the industrial scale [41,42] and has the advantages such as low cost, continuous operation and short processing time. A distinctive feature of the method is that it can produce porous microspheres of various composition without template and ensure homogeneous composition distribution in the spheres [43]. This type of porous microspheres is desirable for photocatalytic applications due to their large surface area, flexible composition, and easy handling properties [44,45]. Under solar light irradiation, $Nb-TiO_2/WO_3$ microspheres showed higher photocatalytic activity for the photodegradation of aqueous methylene blue solution compared with that of pure TiO_2 microspheres and Nb doped TiO_2 microspheres.

2. Experimental

2.1. Chemicals

Titanium tetrachloride ($TiCl_4$, 99.0%), ammonia solution ($NH_3{\cdot}H_2O$, 2.5%), hydrogen peroxide (H_2O_2, 30%), niobium oxalates ($C_6H_{12}N_3NbO_{13}$, 99.95%) and ammonium tungstate hydrate ($H_{40}N_{10}O_{41}W_{12}{\cdot}xH_2O$) were purchased from Shanghai Chemical Co. Methylene blue was obtained from Tianjing Chemical Co. All chemicals were chemical grade and used without further purification. Distilled water was used in all experiments.

2.2. Preparation of catalysts

7.9 mL $TiCl_4$ liquid was carefully diluted with ice water and a transparent colorless aqueous solution ($0.36\ mol\ L^{-1}$) was prepared. This solution was further diluted by 450 mL of water and a white precipitate was obtained by adding 50 mL of ammonia solution (2.5% w/w) dropwise. The white precipitate was washed with distilled water for three times in order to remove residual chlorine ions. The as-prepared white precipitate was added into a mixed aqueous solution containing 100 mL of H_2O_2 solution (30% w/w) and 400 mL of distilled water and a transparent orange solution of peroxotitanium with pH 4 was obtained. Then, niobium oxalate of calculated amount was dissolved in the orange transparent solution of peroxotitanium, and the pH of solution was adjusted to 4 again with ammonia solution.

The as-prepared solution was atomized by an ultrasonic nebulizer and the formed mist was passed through a high temperature quartz tube in the flow of O_2 at the temperature of 800 °C. Powders were formed by pyrolysis of precursor solution and they were collected with an electrostatic collecting device connected to the end of the quartz tube. The 5 mol% Nb-doped TiO_2 ($Nb-TiO_2$) was obtained by ultrasonic spray pyrolysis method. For comparison, pure TiO_2 sample was also prepared by the same method. Finally, the as-prepared pure TiO_2 and niobium doped TiO_2 samples were annealed at 550 °C for 1 h in air. Nb-doped TiO_2 microspheres modified with tungsten oxide were obtained by dispersing the above-mentioned $Nb-TiO_2$ powders in aqueous solution of ammonium tungstate hydrate at a 1% molar ratio of W to Ti. The obtained suspension was dried at 70 °C to evaporate the solvent, and the residual powder was annealed at 500 °C for an hour.

2.3. Characterization

X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku, D/max-2500 X-ray diffractometer. Morphology and composition analysis were performed on a FEI quanta 250 field emission scanning electron microscopy (FESEM) equipped with a energy dispersive X-ray (EDX) analysis accessory. High-resolution electronic micrographs were acquired using a JEOL JEM-2100 transmission electron microscope (TEM) operated at an acceleration voltage of 200 kV. UV–vis diffusion reflectance (DR) spectra of the samples were recorded on a Lambda 900 UV–Vis–NIR spectrophotometer and $BaSO_4$ was used as a reference. N_2 adsorption/desorption isotherms were measured at 77 K using a Micromeritics ASAP 2010N analyzer. Specific surface areas were calculated using the BET model. Pore size distributions are evaluated from adsorption branches of nitrogen isotherms using the BJH model. Photoluminescence (PL) spectra were recorded with a Jobin Yvon HR800 micro-Raman spectrometer using a 325 nm line from a He-Cd laser as excitation source.

2.4. Photocatalytic reaction

Methylene blue (MB) was used as the model pollutant in the photodegradation experiments. A 150 W xenon lamp (Hayashi UV410) was used as light source and its output intensity was set at $84\ mW\ cm^{-2}$. The Xe lamp irradiation simulated solar light in the ultraviolet and visible spectral region, but cutoff the infrared part with a built-in filter. To obtain pure visible irradiation, a longpass filter (FC42, Fujifilm) was combined with the Xe lamp whose cutoff wavelength was 400 nm. 0.1 g photocatalysts were added into 100 mL of MB solution with an initial concentration of 10 mg/L. The solution was stirred in the dark for about 30 min to obtain a good dispersion and establish adsorption–desorption equilibrium

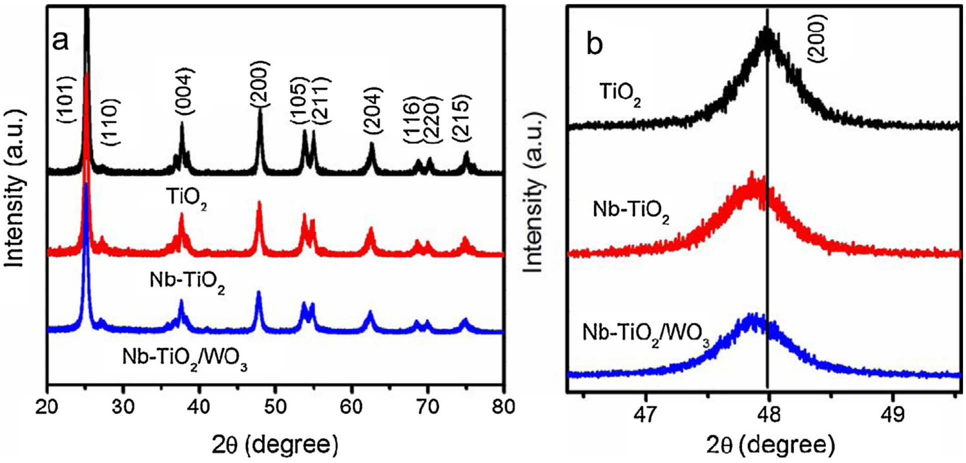

Fig. 1. (a) XRD patterns and (b) magnified XRD patterns in the region between 47° and 49° of TiO_2, $Nb-TiO_2$ and $Nb-TiO_2/WO_3$ microspheres.