



Research paper

A synergetic effect of ytterbium-doping and ammoniation on enhancing UV and visible photocatalytic activities of TiO₂Lei Ma^{a,*}, Jinhua Ren^b, Chi Zhang^a, Fei Hu^a, Zhiquan Zhou^a, Wenjie Zhou^a, Yuchen Zhang^a, Ming Lu^{a,*}^a Department of Optical Science and Engineering, Shanghai Ultra-Precision Optical Manufacturing Engineering Center, Fudan University, Shanghai 200433, China^b Department of Materials Science, Fudan University, Shanghai 200433, China

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ABSTRACT

A synergetic effect of rare earth (Yb) ion doping and ammoniation on the enhancements of both ultraviolet and visible photocatalytic activities of TiO₂ is reported. It is found that ammoniation can dope both nitrogen and hydrogen ions for bandgap narrowing and dangling bond passivation, respectively. Meanwhile, the Yb-doping results in the formation of defective bands that are close to the conduction band minimum, and have strong electron capture abilities to prevent recombination of photogenerated electrons and holes. The synergism of the two effects of Yb doping and ammoniation leads to a significant enhancement of both ultraviolet and visible photocatalysis.

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1. Introduction

Photocatalytic applications such as water splitting for hydrogen acquisition and decomposition of organic molecules for environmental protection have aroused broad interests [1–3]. However, the requirement of wide bandgap width of photocatalyst for redox reaction at the surface limits the wavelength range of light available for photocatalysis to the ultraviolet (UV) regime. Unfortunately, the proportion of UV regime is rather low in the solar emission spectrum on the ground [1–3]. To extend the photoactivity to the visible regime, bandgap engineering of photocatalyst has been proposed via doping photocatalyst with metal [4,5] or non-metal [6–8] ions, aiming at introducing intermediate levels and/or narrowing the bandgap width.

In terms of metal doping, rare earth (RE) ion doping into wide-bandgap photocatalyst such as TiO₂ has proven efficient to improve the photocatalytic property by modifying the bandgap [9–14]. For instance, Yb-doped TiO₂ can not only suppress the recombination of photogenerated electron and hole pairs, but also broaden its spectrum absorption range with its high oxidizability remained [15–18]. On the other hand, doping with non-metal element such as N, F, C or S [2,3,6–8] into TiO₂ could narrow the bandgap width, too, and extend the absorption wavelength to the visible light regime. Among these, N stands out as the most promising candidate due to its comparable ionic radius close to

that of O, making N 2P state effectively merge with O 2P state [19–23]. Traditionally N-doping was realized by chemical synthesis, which could introduce impurities and bandgap narrowing would not be achieved [24]. Recently, a new approach of high-pressure ammoniation has been proposed [25–27]. Ammoniation can dope both nitrogen and hydrogen ions for bandgap narrowing and dangling bond passivation, respectively, and enhance both UV and visible photocatalytic activities of TiO₂ [25–27].

Although Yb-doped TiO₂ and ammoniated TiO₂ have shown better performance in photocatalysis, the synergetic effect of Yb-doping and ammoniation has been rarely studied. If these two methods are applied together, a synergetic effect may work and further enhance the photocatalysis, as expected. In this work, we study the synergism of non-metallic ion doping (nitrogen and hydrogen ion doping via ammoniation) and rare earth ion (Yb) doping to enhance both the UV and visible photocatalytic activities of TiO₂.

2. Experimental

2.1. Materials

The photocatalyst TiO₂ was prepared by magnetron sputtering method. The films were prepared on a magnetron sputtering system (Beijing Shengdeyu, SY-500). The titanium sputtering target was from Znxcmaterial with purity of 99.99%. The base pressure of the sputtering chamber was less than 2.0×10^{-3} Pa. Sputtering was conducted in a pressure of 0.82 Pa ($P_{O_2}/P_{Ar} = 1/40$) at room temperature. The sputtering power was set at 300 W (around 10

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W/cm²), which yielded a deposition rate of 2.5 nm/min. TiO₂ film was grown on a quartz substrate (two-side polish, 10 × 10 × 0.2 mm³ in size), followed by heating in nitrogen at 600 °C for 2 h. The sputtering time was one hour, and all the sample thicknesses were 150 nm.

2.2. Synthesis of different TiO₂ samples

The Yb-doped TiO₂ or “TiO₂:Yb” was also prepared by the magnetron sputtering method. The sputtering target was composed of TiO₂ and Yb₂O₃ (TiO₂/Yb₂O₃ = 100/1 wt%, 99.99% purity) from Znxc-material. The magnetron sputtering and annealing conditions were the same as above. The “TiO₂:Yb” film was formed with a stable crystalline structure.

For ammoniation, the TiO₂ and “TiO₂:Yb” samples were placed in the chamber of autoclave, and then subjected to a 20.0 bar NH₃ atmosphere at 400 °C for 24 h, the samples are termed “TiO₂-NH₃” and “TiO₂:Yb-NH₃”, respectively.

2.3. Characterization methods

The surface morphology was examined using an atomic force microscope or AFM (PSIA, model X-100) in non-contact mode. Optical absorption spectra were recorded at room temperature with a UV-Vis-NIR spectrophotometer (Tianjin Gangdong, WGD-8/8A) in an incident-light scanning mode. To measure the inter-

band photoluminescence (PL) emission of TiO₂, the TiO₂ samples were excited with λ = 325 nm laser beam from a CW He-Cd laser (Melles Griot, Series 74). The PL spectra were recorded with an intensified charge-coupled device (ICCD) (Andor Technology, iStar DH720). The crystal structures of TiO₂ were examined by Raman spectroscopy (Horiba Jobin Yvon, XploRA microRaman system). Chemical compositions of the samples were analyzed using X-ray photoelectron spectroscopy (Ulvac Japan, PHI 5000 Versaprobe). All binding energies were referenced to the C 1s peak (284.6 eV) arising from adventitious carbon.

2.4. Evaluation of photocatalytic activity

To evaluate the photocatalytic activity of TiO₂, photo-decomposition of methylene blue (MB) was used. Absorption spectra of MB solutions loaded with or without TiO₂ were recorded. The concentration of MB was 0.01 mmol/L. A 400 W mercury lamp (Heraeus, MDQ 401SE) equipped with various filters served as a light source. After filtering, the lights with wavelengths centered at λ = 365 and 405 nm were used as UV and visible light sources, respectively. The UV light power is 15.5 mW and the visible one is 87.8 mW. Photo-decomposition of MB by TiO₂ was performed in a cuboid quartz vessel. In a photocatalysis test, 2.0 mL MB solution was added into the quartz vessel, which was aerated with an oxygen flow of 6 mL/min. The amount of volatilization of aerated MB solution was less than 5% after 8 h UV or visible illuminations.

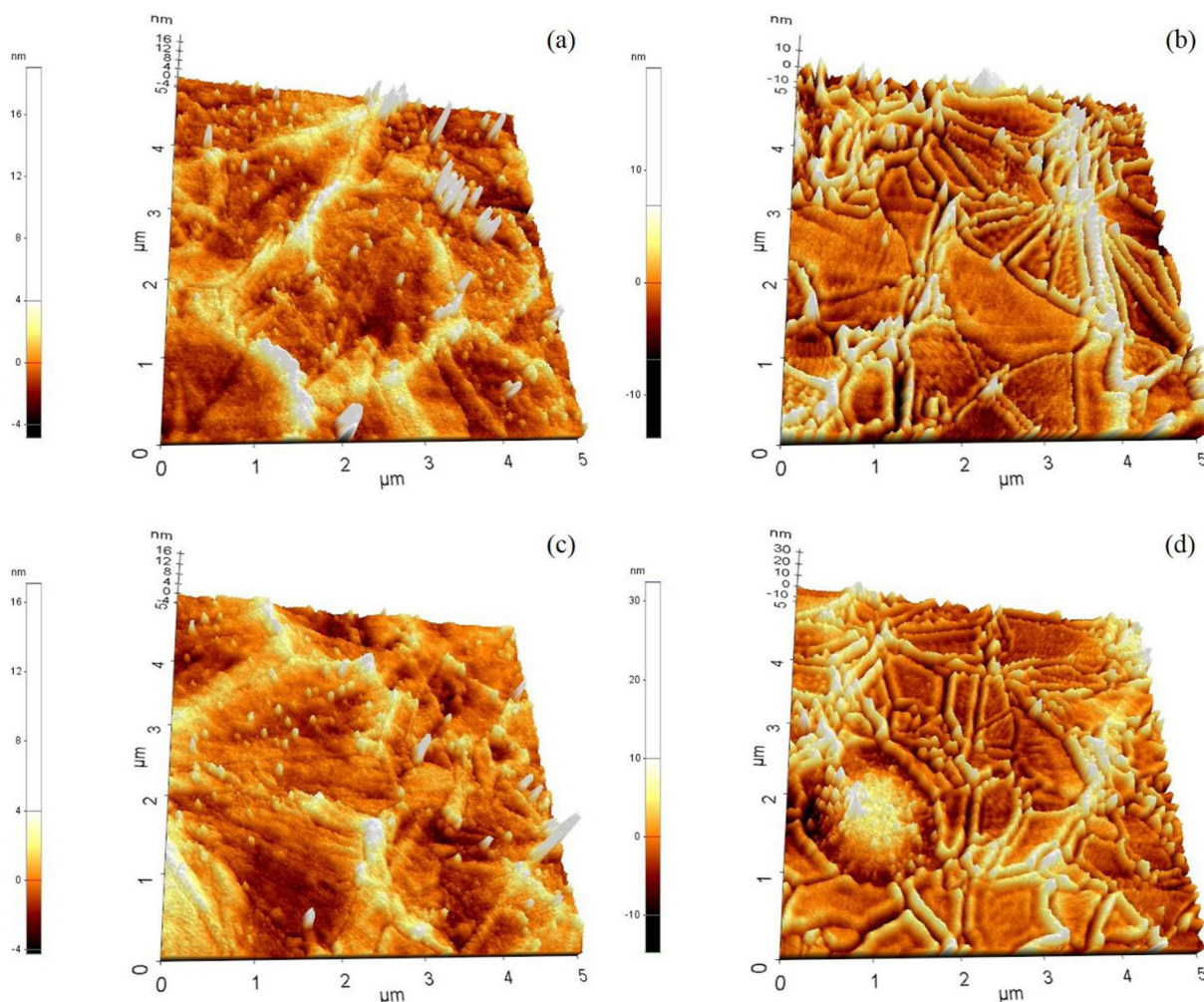


Fig. 1. AFM images of TiO₂ that have been untreated (a), doped with Yb ions (b), ammoniated (c) and doped with Yb ions and then ammoniated (d).

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