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Full Length Article

Oxygen vacancy-mediated efficient electron-hole separation for C-N-S-tridoped single crystal black TiO_2(B) nanorods as visible-light-driven photocatalysts

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ABSTRACT

In-situ oxygen vacancy-mediated C-N-S-tridoped single crystal black TiO_2(B) nanorods are smoothly manufactured. The sample preparation is divided into two steps, first of all, a simple hydrothermal process, followed by an in-situ solid-state chemical substitution method with calcination at 500 °C. We have a number of representations of the catalyst such as crystallinity, morphological structure, etc. by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, and UV–vis diffuse reflectance spectroscopy, respectively. This b-C-N-S-TiO_2(B) has the advantages of Oxygen Vacancy, single crystal structure of nanorods, Ti^{3+} self-doping, C-N-S-tridoped, so this sample band gap is narrow. Moreover, through the reduction of phenol and Cr(VI), we know the photocatalytic performance of the b-C-N-S-TiO_2(B), the reduction efficiency of phenol and Cr(VI) is ~6.1 times and ~7 times of no doping samples, respectively, under visible light illumination. The predominant photocatalytic performances because of the synergetic action of Ti^{3+} self-doping, C-N-S-tridoped, oxygen vacancy, and the 1D single crystal B phase nanostructure, favoring the separation and transportation of photogenerated charge carriers and the visible light utilization.

1. Introduction

Nowadays, environmental and energy issues are one of the most concerned issues, and the photocatalysis of semiconductors is proposed to solve these problems [1–3]. At the same time, oxygen vacancy can improve the photocatalytic performance of semiconductor, ionic conductivity, charge localization and surface reactivity have great influence on the properties of materials [4,5]. Numerous studies have shown that oxygen vacancies also are semiconductors. Importantly, our recent research shows that the photocatalytic activity of semiconductors mediated by oxygen vacancies is known. Since TiO_2 was proposed in 1972, this semiconductor material has been used as an important photocatalytic material for toxic pollutants in raw water [6,7]. TiO_2 has the advantages of non-toxic chemical stability and low cost [8–11]. But, TiO_2 has a wide band gap, which can only respond under ultraviolet light [12–15]. So many ways to improve it have been proposed.

TiO_2 has four phases, including anatase, rutile, brookite, and TiO_2(B) [16–18]. Among these phases, TiO_2(B) has the advantages of long cycle length, high safety and minimal environmental impact [19,20]. So it has the most extensive use, such as lithium batteries and photocatalysts [21,22]. Marchand et al. first synthesized TiO_2 (B) in 1980. Since then, the calcination method of titanium dioxide is widely used in various forms, such as nanorods, nanowires, nanobelts, nanotubes as well as nanobelts [10,23]. Compared with other morphologies, the TiO_2(B) nanorods have good photocatalytic performance and electrochemical properties, and can provide direct transportation route for electron transfer, and it can inhibit the recombination of the electron hole pair. The results show that the electron hole' s recombination that could lead to the low photocatalysis efficiency. Therefore, it is proposed to decrease the band gap and suppress the recombination of photogenerated electron hole pairs [24–27].

In addition, there are many ways to improve the photocatalytic performance of TiO_2(B) such as metal and non-metallic doping, surface plasmon resonance, and so on [28–30]. Among these methods, metal and non-metallic doping and trivalent titanium doping are relatively simple and effective methods [31]. Compared with metal doping, non-metallic doping is more effective and environmentally friendly, and its thermal stability is lower [32,33]. Specially, C-N-S-tridoped TiO_2(B) (CNST) can significantly improve the visible light absorption properties by inserting the C-N-S into the lattice of TiO_2(B), it can create a hybrid orbital above the valence band (VB) of TiO_2 (the overlap of oxygen 2p states and nitrogen 2p states), and narrow the band gap through the

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overlap of sulfur 3p states and oxygen 2p states, thus showing an enhanced visible light photocatalytic performance [34–36]. Moreover, C-doped TiO_2(B) achieves the same purpose because a hybrid orbit can be formed above the VB of TiO_2 by replacing lattice Ti atom or lattice O atom with carbon atoms. Therefore, it is still a challenge to use the advantages of three different non-metals dope TiO_2(B) to improve the photocatalytic activity [37–39]. So, we think that the preparation of CNST nanorods can improve the photocatalytic performance through doping with C, N and S atoms [40,41]. At the same time, it is found that b-C-N-S-TiO_2(B) (bCNST) nanorods can broaden the absorption of visible light and improve the catalytic performance [42]. The prepared bCNST effectively reduces the width of the band gap and inhibits the rapid recombination of the electron hole pair, which shows excellent photocatalytic performance under visible light. Since then, many efforts have been devoted to the synthesis of Ti^{3+} self doped TiO_2 because of its transformation from ultraviolet absorption to visible and near infrared region. Various methods have been used to synthesize black or gray TiO_2, including high pressure, high Al vapor reduction plasma assisted hydrogenation, laser treatment, hydrogenation, and chemical reduction. Among these methods, high pressure and hydrogenation are unsuitable for practical application. It has been noticed that in situ reduction treatment by using $NaBH_4$ is an effective route to achieve the synthesis of Ti^{3+} self doped TiO_2, because of the advantages of simple process and low cost.

Based on the above said, we prepared the oxygen vacancy-mediated CNST black single-crystalline nanorods by a simple hydrothermal method. It was great for enhancing photocatalytic activity to degrade phenol, aromatic phenol and other toxic phenol under visible light. In addition, photocurrent density was improved significantly. This paper further introduces the photocatalytic performance and mechanism of reaction.

2. Materials and methods

2.1. Materials

Materials include butyl titanate (TBOT), anhydrous ethanol (EtOH), NaOH, glacial acetic acid (HAC, 99.5%). Cystine was from the chemical reagents Co., Ltd. of Tianjin, China. Sodium borohydride ($NaBH_4$, 98%) is bought by Aladdin from reagent company in China. All the chemicals that are used in this work are analytical grade, and can be used without purification at a more advanced level. Deionized (DI) water is made use of throughout the whole study.

2.2. Preparation of photocatalysts

The synthesis of TiO_2(B) is based on previous articles [43]. The C-N-S-tridoped single crystal TiO_2(B) was checked via the brief hydrothermal method. In detail, the 0.5 g of cysteamine is treated by HNO_3, which was diluted (1:2) for 2 h. Then 2 g of TiO_2(B) was added in the suspension with continuous stirring. Then put the product into 100 ml Teflon sealed autoclave and heat it for 180 °C, 4 h. It denoted as CNST. The black CNST was obtained by $NaBH_4$ reduction through the method of previous reports, the black CNST was prepared. The complete synthesis process diagram is shown Fig. 1.

2.3. Characterization

The test of X-ray diffraction was carried out on XRD-D8 Advance, Bruker. The FE-SEM, HitachiS-4800 and TEM JEOL JEM-2010 were used to test the structure and morphology of the samples with an accelerating voltage of 200 kV. The elements of the sample were analyzed with the spectrometer X-ray photoelectronspectroscopy (Kratos-ULTRA AXIS DLD systemwith Al Kα X-ray source). The indeterminate carbon on the surface of 284.6 eV serves as a reference for all binding energies. The light absorption range of the sample was measured by ultraviolet spectrophotometer (TU-1901spectrophotometer). The $BaSO_4$ was used as the background ranging from 190 to 800 nm. The electrochemical impedance spectroscopy (EIS) were recorded by a computer-controlled IM6e Impedance measurement unit (ZahnerElektrik, Germany).

2.4. Photocatalytic test

Photocatalytic reduction of phenol: the photocatalytic activity of the prepared samples was studied by reducing phenol. 350 W xenon lamp equipped with optical filter (lambda = 420 nm) is a simulation of visible light. All the tests were carried out at RT (20 + 2 °C). The photocatalytic experiment was carried out under visible light; the phenol 20 mg of the photocatalyst added to 30 ml of the phenol ($10\,mg\,L^{-1}$) and then placed in a 50 ml cylindrical quartz glass kettle with a water cycle equipment. Before illumination, the mixed solution was magnetic stirring for 30 min under the environment of the darkness to achieve the adsorption/desorption equilibrium. During the specific process of visible light photocatalytic reaction, which every takes up about 30 min, the sample was centrifuged and the absorbance of the sample was studied by the SHIMADZU model UV-2550 spectrophotometer (lambda = 553 nm) so ad to calculate the photocatalytic reduction rate of phenol.

Cr (VI) photocatalytic reduction: firstly, the $5\,mg\,L^{-1}$ is dissolved in the $100\,mg\,L^{-1}$ solution and dissolved in water. Then, a 35 mg Cr(VI) and 20 mg photocatalyst was added to the quartz reactor. The reactor is placed at a distance of 20 cm from the light source. After stirring in the dark for 30 min, the adsorption and desorption equilibrium of the prepared photocatalyst was measured, and the system irradiated the 420 nm cut-off filter 300 W xenon lamp under visible light. At a certain time interval, about 5 ml dispersed centrifugation, extract and filter, T6 UV–vis spectrophotometer at k = 540 nm for the determination of Cr (VI) concentration, the method of using 1,5-diphenylcarbazide for the ultraviolet visible spectrophotometer is developed and promoted.

2.5. Photoelectrochemical test

The photoelectric measurement (CHI760E, Shanghai) was studied by electrochemical workstation. The AM- 1.5 solar system is used as the simulated daily light source. The standard three-electrode system is made of conductive glass electrode, Ag/AgCl reference electrode and platinum foil as the opposite electrode. The 1 M KOH aqueous solution is used as the electrolyte. For the preparation of electrodes, 100 mg of samples were dissolved in 2 ml of alcohol solution under magnetic stirring. The mixed coating impregnated with $1 \times 2\,cm^2$ FTO glass electrodeat calcined at 350 °C for 1 h, ensures good electrical contact in Ar.

3. Results and discussion

The crystallinity and crystallinity of the prepared samples have a great impact on the performance of photocataly, determining its practicability in practical applications [44]. Under this kind of condition, the phase structure and degree of crystallinity of the prepared samples are analyzed by X ray diffraction (XRD), as shown in Fig. 2a, the main diffraction peaks are known as 14.2, 24.9, 28.6, 43.9 and 48.4°, respectively, corresponding to the crystal surface of (0 0 1), (1 1 0), (0 0 2), (0 0 3) and (0 2 0) TiO_2(B) [45]. Compared with the original TiO_2(B), the peak of C-N-S-TiO_2 (B) has a slight change, but it does not affect its structure and performance. Similarly, the peak of the black sample has been slightly c-hanged. For (bCNST), the reduction and expansion of bCNST diffraction peaks and the change of crystal structure may be related to the existence of oxygen vacancy and Ti^{3+}, resulting in a slight decrease in the lattice and lattice size of chaos [46].

The absorption of visible light can also enhance photocatalysis. In order to explore the range of light absorption of the sample, the light absorption and band gap of the sample were evaluated by UV–vis