氟掺杂 TiO₂ 纳米管的可见光催化活性及第一性原理计算苏雅玲^{1,2,*} 李 轶³ 杜瑛珣¹ 雷乐成^{2,*}

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摘要: 作为光催化技术的核心, 提高 TiO₂ 的光催化活性和对可见光的利用率是当前光催化研究中最重要研究课题. 为了提高 TiO₂ 纳米管的可见光催化活性, 采用化学气相沉积法对 TiO₂ 纳米管进行了氟掺杂. 扫描电子显微镜(SEM)结果表明退火温度对于 TiO₂ 纳米管的形貌完整性有较大影响, 当样品在 550 和 700 °C 下退火, 氟掺杂 TiO₂ 纳米管结构受损; X 射线衍射(XRD)分析表明氟掺杂对 TiO₂ 由锐钛矿相转化为金红石相有阻碍作用; X 射线光电子能谱(XPS)测试表明化学气相沉积能有效地对 TiO₂ 纳米管进行非金属掺杂, 且该方法安全、操作简单. 氟掺杂 TiO₂ 纳米管对甲基橙有较高的可见光催化降解活性. 第一性原理计算结果表明氟掺杂对 TiO₂ 带隙无显著影响, 费米能级附近的 F 2p 轨道电子位于价带底部, 与 O 2p 交联作用较小, 因此对 TiO₂ 光吸收带边影响不大. 氟掺杂能促进表面氧空穴的产生, 增加表面酸度与 Ti³⁺, 有利于减少电子-空穴复合率, 从而提高其光催化活性.

关键词: TiO₂ 纳米管; 氟掺杂; 可见光; 催化活性; 电子结构

中图分类号: O647; O649

Visible-Light-Driven Catalytic Properties and First-Principles Study of Fluorine-Doped TiO₂ NanotubesSU Ya-Ling^{1,2,*} LI Yi² DU Ying-Xun¹ LEI Le-Cheng^{2,*}

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Abstract: Improving the photocatalytic activity and the utilization of visible light of TiO₂ is the most important research topics in the photocatalytic field. To improve the photocatalytic activity of TiO₂, we used chemical vapor deposition (CVD) to dope TiO₂ nanotubes with fluorine. Scanning electron microscopy (SEM) images showed that the annealing temperature significantly affected the morphological integrity of TiO₂ nanotubes. Upon annealing at 550 and 700 °C, the structure of F-doped TiO₂ nanotubes suffered from an observable disintegration of morphological integrity. X-ray diffraction (XRD) results indicated that the F impurity retarded the anatase-rutile phase transition. Fluorine was successfully doped into TiO₂ by CVD, as indicated by the X-ray photoelectron spectroscopy (XPS) results. F-doped TiO₂ nanotubes showed higher photocatalytic activity. First-principles calculations suggested that the F 2p states were located in the lower-energy range of valence band (VB) and less mixed with O 2p states. It thus contributed little to the reduction of the optical band gap. This is consistent with the finding that the band gap of F-doped TiO₂ is very close to that of undoped TiO₂. Therefore, the higher catalytic activity of F-doped TiO₂ should be

Received: November 1, 2010; Revised: January 20, 2011; Published on Web: February 24, 2011.

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The project was supported by the Fund of the State Key Laboratory of Hydrology-Water Resources and Hydraulic Engineering, Hohai University, China (2009490911) and National Natural Science Foundation for Young Scientists of China (20906097).

河海大学水文水资源与水利工程科学国家重点实验室开放研究基金(2009490911)与国家自然科学基金青年基金(20906097)资助项目

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attributed to the creation of surface oxygen vacancies upon F-doping, which enhances surface acidity and increases the amount of Ti^{3+} ions.

Key Words: TiO_2 nanotubes; Fluorine-doping; Visible-light; Catalytic property; Electronic structure

1 Introduction

Photocatalytic technology is an effective and promising method for the removal of pollutants with low concentration in water.¹ TiO_2 is considered as the most attractive photocatalyst due to its excellent photocatalytic properties, stability, low cost, and nontoxicity.² However, it can be activated only by UV light because of its large band gap of 3.2 eV, which hampers its widespread application. Therefore, it is of special interest to extend its optical response to the visible range. It has been reported that doping TiO_2 with nonmetal such as N,^{3–5} C,^{6,7} S,^{8,9} and I^{10,11} can activate its visible-light activity. Asahi *et al.*³ have carried out first-principles calculations and demonstrated that N-doped TiO_2 can enhance the photoactivity under visible irradiation, owing to band-gap narrowing. A few researchers have also reported the improvement of photocatalytic activity by F-doped TiO_2 under UV or visible irradiation.^{12–14} However, some researches suggest that F-doping has no effect on the absorption edge of TiO_2 ^{13,14} and the optical absorption of TiO_2 .^{15,16} Actually, the doped F atoms can convert Ti^{4+} to Ti^{3+} by charge compensation, and the presence of a certain amount of Ti^{3+} reduces the electron-hole recombination rate and thus enhances the photocatalytic activity.¹³

Presently, TiO_2 nanotubes prepared by electrochemical anodization are gaining more attention for their high specific surface area.^{17–28} This novel supported tubular structure of TiO_2 possesses good mechanical adhesion strength and electronic conductivity because it is directly grown from titanium metal substrate. So it is a promising electrode for application in photoelectrocatalytic process. Recently, it is reported that using heat treatment in ammonia²⁶ or ion implantation^{29,30} can dope nitrogen into TiO_2 nanotubes. For the first method, the variety of doping elements is limited by the gas sources. For the second one, ion implantation is complicated and expensive. Therefore, a simple, safe, and effective nonmetal-doping method is of special interest. Besides, the mechanism of nonmetal-doping of TiO_2 and the doping effect on the photocatalytic activity under visible irradiation still deserve further investigation.

In this work, the objective is to prepare visible-light-active F-doped TiO_2 nanotubes with high surface area, and elucidate the mechanism of the higher photocatalytic activity of F-doped TiO_2 nanotubes under visible irradiation. TiO_2 nanotubes were fabricated by anodization of Ti in $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O} + \text{NH}_4\text{F}$ electrolyte, followed by chemical vapor deposition (CVD) treatment to perform F-doping. CVD is low-cost, easy to manipulate and widely used for direct deposition on specific structures and substrates.³¹ NaF was selected as the precursor to be the source of

F dopant. The samples were characterized and their photoelectrochemical properties under visible light were investigated. Furthermore, we calculated and compared the electronic structures of undoped and F-doped anatase and rutile TiO_2 by the supercell approach based on the first-principles.

2 Experimental

All chemicals were analytical grade and used without further purification. Titanium sheets (99.60% purity) were degreased in an ultrasonic bath with acetone (99.5% purity), rinsed in deionized water and dried in air at room temperature. Anodization experiments were performed in a cylindrical electrochemical reactor using a direct current (DC) power supply. Titanium sheet served as anodic electrode and nickel sheet as the cathode. Titanium sheet was anodized at 20 V for 1 h in $1/12 \text{ mol} \cdot \text{L}^{-1} \text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (99.5% purity) containing 0.5% (w, mass fraction). NH_4F (96% purity). Anodization was carried out at room temperature ($(20 \pm 1)^\circ\text{C}$) with magnetic agitation. Then as-anodized TiO_2 nanotubes was put into the central quartz cannula in a resistor furnace (Hangzhou LanTian Instrument Co. Ltd.), and dehydrated in a stream of dry nitrogen at 300°C for 30 min. Meanwhile, $50 \text{ g} \cdot \text{L}^{-1}$ NaF (95% purity) solution was heated in the thermostatic water bath at 80°C . When the temperature in the thermostatic water bath stabilized, fluorine-containing vapor was transported into the furnace by N_2 with a carrier gas flow rate of $3300 \text{ mL} \cdot \text{min}^{-1}$. Annealing temperature was 400, 550, and 700°C , respectively. At the end of CVD, the reactor was purged by nitrogen gas for about 30 min. The sample was annealed for 2 h, and then removed from the furnace. The sample was rinsed in deionized water. For comparison, undoped sample was obtained by annealing in an air atmosphere at 700°C for 2 h.

For a morphology characterization of F-doped TiO_2 nanotubes, a field-emission scanning electron microscopy (FE-SEM, JSM-5600LV, Netherlands) was used. The crystal structures of the samples were identified by X-ray diffraction (XRD, Rigaku, D/max-rA, Japan) using a diffractometer with Cu K_α radiation. The elemental composition of F-doped TiO_2 nanotubes was determined by X-ray photoelectron spectroscopy (XPS, Perkin Elmer, a RBD upgraded PHI-5000C ESCA system, the United States). Binding energies were calibrated by using the containment carbon C 1s (284.6 eV).

The catalytic activity of F-doped TiO_2 nanotubes electrode was evaluated by the degradation of methyl orange (MO, 96% purity) solution. The photoelectrocatalytic degradation under a visible light irradiation was carried out under the following

conditions: under visible light irradiation (a 300 W Xe lamp, Shanghai HuaLun Light) with any irradiation below 400 nm removed by 2 mol · L⁻¹ NaNO₂ (99% purity) solution,³² vigorous bubble, 0.1 mol · L⁻¹ sodium sulfate as electrolyte, and 1.0 V anodic bias potential was applied. The initial concentration of MO was 10.0 mg · L⁻¹ (denoted as C₀), and the concentration of MO during reaction (denoted as C) was monitored at the absorption wavelength of 463 nm by a TECHCOMP 8500 spectrophotometer.

The electronic structures of F-doped TiO₂ were carried out by CASTEP modules based on the density functional theory (DFT).³³ The plane-wave all electron basis sets method was used to optimize crystal geometries and to obtain the corresponding electronic band structures. The initial geometry configurations were optimized and the convergence was set to 1.0 × 10⁻⁵ eV · atom⁻¹ for total energy difference. The energy cutoff was chosen as 340 eV. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation function³⁴ was used. The core electrons were replaced by the ultrasoft core potentials. Anatase and rutile TiO₂ were used to construct models for calculation. In the calculations, 24-atom 2 × 1 × 1 supercell was used to construct the anatase and rutile F-doped structures, respectively. To set the doped models, one oxygen atom in the supercell was replaced with a fluorine atom for F-doped TiO₂ model.

3 Results and discussion

Fig.1 shows SEM images of TiO₂ nanotubes before and after F-doping. It is clear that the diameter of TiO₂ nanotubes was

Fig.2 XRD patterns of TiO₂ nanotubes at different annealing temperatures

approximately 35 nm before doping, and the value was about 95 nm after doping. So, F-doping has an effect on the diameter of TiO₂ nanotubes. After annealing in F-containing vapor at 400 °C for 2 h, the nanotubular structure keeps its integrity with no significant morphological change. However, the structures of the other three samples annealed at 550 and 700 °C suffers from an observable disintegration of morphological integrity. This structural damage is similar to the SEM images of previous reports on N-doped TiO₂ nanotubes by ion implantation.³⁰ Consequently, annealing temperature during CVD has a significant effect on the morphological integrity of TiO₂ nanotubes.

Fig.2 shows XRD spectra of F-doped TiO₂ nanotubes annealed at 400, 550, and 700 °C for 2 h in F-containing vapor through CVD, and undoped TiO₂ nanotubes annealed at 700 °C

Fig.1 SEM images of TiO₂ nanotubes before and after F-doping

(a) undoping (700 °C); (b) F-TiO₂ (400 °C); (c) F-TiO₂ (550 °C); (d) F-TiO₂ (700 °C)

for 2 h in air, respectively. For both undoped and F-doped samples, after annealing at 400 °C, the structure consists of only anatase. While after annealing at 550 and 700 °C, the mixture of anatase and rutile phase appeared. The rutile content increased with the increase in the annealing temperature. Besides, it can be seen that the rutile content in undoped sample is higher than that in F-doped sample when annealing at the same temperature. This difference indicates that F impurity retards anatase-rutile (A-R) phase transition. This conclusion is identical with that reported by other researchers.^{12,14} Although the ionic radius of F⁻ (0.136 nm) is close to that of O²⁻ (0.140 nm), the substitution of the former for the latter in unit cell causes a lattice distortion and accumulates strain energy, consequently hampers the A-R transition.³⁵

Determination of the oxidation state of the doped F is carried out by measuring F 1s binding energy (E_B) with high-resolution XPS spectrum, as shown in Fig.3(a). It is observed that an unsymmetrical F 1s peak consists of a few obvious tailing peaks. This means that different chemical forms of F atoms may exist in TiO₂. Therefore, the F 1s peak is deconvoluted into two separated peaks with Gaussian distributions. The peak at 686.4 eV of F 1s is originated from the F atoms of the TiOF₂.¹³ The peak at 688.5 eV can pertain to Ti—F bonds,^{36,37} indicating that the substitutional F atoms occupied oxygen sites in the TiO₂ crystal lattice. The position of this peak is close to the value reported by Yu *et al.*¹² for the substitutional F atoms in TiO₂. These results indicate that F atoms are doped in-

to TiO₂.

Fig.3(b) shows that the peak at 460.4 eV can pertain to Ti 2p_{3/2}, and the other peak at 466.1 eV is attributed to Ti 2p_{1/2}, indicating that Ti ions are in an octahedral environment and the valence states are not influenced by F-doping.³⁸ Moreover, the binding energy of peak at 460.4 eV is larger than the standard value ((458.0±0.1) eV).³⁹ This suggests that F-doping can influence the surroundings of Ti atoms, that is, F atoms can adsorb the electrons of Ti atoms, increasing the binding energy of the electrons of Ti 2p, and thus the surface acidity of TiO₂ is enhanced.¹³ Li *et al.*¹³ measured acetaldehyde amounts adsorbed on F-doped TiO₂ powders and pointed out that F-doped TiO₂ with a strongly acidic surface adsorbed more acetaldehyde molecules compared with pure TiO₂.

Fig.4 shows the photoelectrocatalytic efficiencies of F-doped TiO₂ nanotubes annealed at 400, 550, 700 °C, and undoped TiO₂ nanotubes annealed at 700 °C under visible light irradiation. The catalytic activity of F-doped TiO₂ nanotubes was evaluated by the degradation of methyl orange (MO) solution. The initial concentration of MO was 10.0 mg · L⁻¹. It is apparent that the undoped TiO₂ nanotubes show rather low photoelectrocatalytic activity, as it achieves a reduction of only 8.2% of MO concentration in 120 min. F-doped sample (700 °C) had the higher photoelectrocatalytic efficiency, achieving a reduction of 84.5% of MO concentration, higher than F-doped samples annealed at 400 °C (27%) and 500 °C (66.9%). The higher catalytic efficiency of F-doped samples indicates the positive effect of F-doping on the photoelectrocatalytic activities. The higher photoelectrocatalytic efficiency of F-doped (700 °C) is attributed to its higher content of rutile phase. Since it is easier for rutile to be activated to produce the photogenerated electrons and holes, because the band gap energy of rutile TiO₂ (3.0 eV) is lower than that of anatase TiO₂ (3.2 eV).⁴⁰

To explain the effect of F-doping on the visible light photocatalysis of anatase and rutile TiO₂, calculations were performed using the CASTEP code based on the DFT. In the calculations, the supercells with four unit cells were used in con-

Fig.3 (a) F 1s and (b) Ti 2p high-resolution XPS spectra of F-TiO₂ nanotubes

Fig.4 Catalytic activity of F-TiO₂ nanotubes for the degradation of methyl orange (MO) solution annealed at different temperatures under visible light irradiation. The initial concentration of MO was 10.0 mg · L⁻¹.

structing the F-doped structures, where one O atom was replaced by one F atom, as shown in Fig.5.

Fig.6 shows the calculated energy band structures of anatase and rutile of undoped TiO₂ and F-doped TiO₂. The calculated band gap (BG) energy is 2.22 eV for undoped anatase TiO₂, 2.19 eV for F-doped anatase TiO₂, 1.86 eV for undoped rutile TiO₂, and 1.84 eV for F-doped rutile TiO₂. These values are underestimated as a result of the well-known limitation of GGA arithmetic.⁴¹ The BG of F-doping TiO₂ is slightly smaller than undoped TiO₂, with little contribution to the reduction of the optical BG. The doped F atoms can convert Ti⁴⁺ to Ti³⁺ by charge compensation and the presence of a certain amount of Ti³⁺ reduces the electron-hole recombination rate and thus en-

hances the photocatalytic activity.¹³ Moreover, the energy band structures show that doping atom F can provide an occupied energy level in the band gap, and the electron is excited more easily from donor level to conduction band than that from filled band.⁴² The role of impurity can be explained by the fact that doped F atom substituting O results in the addition of a negative charge. The binding energy of this kind of acceptor is small, so the acceptor level near to the conducting band can easily accept electrons. It is interesting to note that the band gap energy of rutile TiO₂ is lower than that of anatase TiO₂ indeed. This result is identical with the higher removal of MO by F-doped TiO₂ under visible irradiation, as shown in Fig.4.

Fig.7 shows the partial density of states (PDOS) of anatase and rutile of undoped TiO₂ and F-doped TiO₂. It can be seen that the conduction band (CB) and the valence band (VB) of undoped anatase and rutile TiO₂ mainly consists of O 2*p* and Ti 3*d* states, indicating some covalence bond character between Ti and O atoms.

For F-doped anatase TiO₂, the dominant contribution to VB is the O 2*p* states mixed with F 2*p*, and the dominant contribution to CB is Ti 3*d*, O 2*p*, and F 2*p* states. Meanwhile, the similar phenomenon can be found in F-doped rutile TiO₂. It is obvious that most F 2*p* states are located in the lower-energy range of the VB bottom, with less mixing with that of O 2*p*, and have little contribution to the reduction of the optical band gap. This is consistent with the result that the band gap of F-doped TiO₂ is very close to that of undoped TiO₂. Therefore, some research-

Fig.5 Cell models of F-doped TiO₂

(a) F-doped anatase TiO₂, (b) F-doped rutile TiO₂

Fig.6 Band structures of TiO₂

(a) undoped anatase TiO₂; (b) F-doped anatase TiO₂; (c) undoped rutile TiO₂; (d) F-doped rutile TiO₂

Fig.7 Partial density of states (DOS) of TiO₂

(a) undoped anatase TiO₂; (b) F-doped anatase TiO₂; (c) undoped rutile TiO₂; (d) F-doped rutile TiO₂

ers believed that F-doping is not a good choice for extending the optical absorption edge of TiO₂ into the visible region.^{13,43} However, Li¹³ and Yang⁴³ *et al.* concluded that F-doping produced several beneficial effects including the creation of surface oxygen vacancies, the enhancement of surface acidity, and the increase of Ti³⁺ ions. In addition, Yang *et al.*⁴³ pointed that the CB bottom was lowered (0.20 eV) more than the VB top (0.16 eV) of F-doped TiO₂. The lower VB top indicates that F-doped TiO₂ has a stronger oxidation power,^{12,14} therefore, F-doped TiO₂ has a higher photocatalytic activity than does undoped TiO₂. Meanwhile, the similar phenomenon can be found in F-doped rutile TiO₂. This calculated electronic structure of rutile unit cell is consistent with the previous report.⁴⁴ Consequently, these above results can elucidate the experiment result that F-doped TiO₂ nanotubes show a higher photocatalytic activity than undoped sample under visible irradiation.

4 Conclusions

In this work, chemical vapor deposition method is applied to dope TiO₂ nanotubes with fluorine atoms to improve their photocatalytic activity under visible irradiation. SEM images show that annealing temperature has a significant effect on the morphological integrity of TiO₂ nanotubes. When annealed at 550 and 700 °C, the structure of F-doped TiO₂ nanotubes suffers from an observable disintegration of morphological integrity. XRD results indicate that F impurity retards anatase-rutile phase transition. Fluorine is successfully doped into TiO₂, as

evidenced from XPS results. Compared with undoped sample, F-doped TiO₂ nanotubes show the higher photocatalytic activity under visible irradiation.

Density functional study on undoped, F-doped anatase and rutile TiO₂ are carried out. The results shows that F 2p states are located in the lower-energy range of the VB bottom, with less mixing with that of O 2p, and have little contribution to the reduction of the optical band gap. This is consistent with the result that the band gap of F-doped TiO₂ is very close to that of undoped TiO₂. F-doping produces several beneficial effects including the creation of surface oxygen vacancies, the enhancement of surface acidity, and the increase of Ti³⁺ ions. Therefore, F-doped TiO₂ nanotubes show a higher photocatalytic activity than undoped sample under visible light irradiation.

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