

N-Doped TiO₂ Nanotube Arrays: Synthesis by Anodization in an Ionic Liquid ([BMIM]BF₄) and Assessment of Photocatalytic Property

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Abstract: N-doped TiO₂ nanotube (NT) arrays were prepared by anodization in electrolytes containing HF, ionic liquid 1-n-butyl-3-methyl-imidazolium tetrafluoroborate ([BMIM]BF₄) and water. The ionic liquid, [BMIM]BF₄, was used as the nitrogen source. The surface morphology and the composition of samples were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR) and UV-Vis diffuse reflectance spectra (DRS). The photocatalytic activities of samples were investigated by the degradation of methylene blue (MB) under spherical xenon lamp. The results show that the degradation rate of MB over N-doped TiO₂ NT arrays is obviously higher than that over undoped TiO₂ NT arrays. The above results are caused by the increased oxygen vacancies and the decreased band gap.

Key words: TiO₂ nanotube array; ionic liquid; N-doped; anodization; photocatalysis

There is tremendous interest in the development of TiO₂ photocatalysis and degradation of organic pollutants. TiO₂ is considered as a highly efficient catalyst to deal with environmental pollution, due to its high photo-stability, non-toxic, low-cost and environmental friendly feature^[1-3]. Recently, TiO₂ nanotubes have been widely used in the photocatalytic field because of their large surface area, strong adsorption capability and high photocatalytic activity compared with the conventional TiO₂ nanopowders and TiO₂ nanofilms^[4-6]. To date, various methods such as anodization^[7,8], sol-gel^[9] and template method^[10] have been developed to prepare TiO₂ nanotube (NT) arrays. Among these methods, the anodization has become a research hotspot, because it is simple, low-cost, easy-to-recovered and straightforward to synthesize self-ordered and well-aligned TiO₂ NT arrays on Ti sheets or films^[11,12].

In recent years, ionic liquid as a new type of green environment-friendly solvent to synthesize inorganic nanoma-

terials attracts great attention^[13,14]. Ionic liquids are room temperature molten salts which consist of large organic cations (containing N or P element) and typically smaller inorganic anions, most of which are imidazole salt, pyridine salt, alkyl ammonium salt, etc^[15,16]. Ionic liquids as reaction media can be widely used in different fields because of their good dissolving ability, wide liquid temperature range, wide electrochemical window, high thermal stability, negligible vapor pressures, less volatile and high ionic conductivity^[17,18]. The first study on Ti anodization with ionic liquids was reported by Schmuki and co-workers^[19]. Wender and co-workers^[20] successfully prepared uniform TiO₂ NT arrays on Ti films in an electrolyte composed of an ethyleneglycol/water (EG/H₂O) solution with [BMIM]BF₄. Misra and co-workers^[21] showed that when Ti sheet was anodized in EG/H₂O solution with 0.6 vol% of [BMIM]BF₄ (EG/H₂O/[BMIM]BF₄), a double-walled TiO₂ NTs structure was obtained. Compared with similar single-walled TiO₂ NTs and commercial TiO₂

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nanoparticles, the double-walled TiO₂ NTs display 2~4 times more photoactivity in terms of hydrogen generation under solar light illumination by the splitting of water. No TiO₂ NTs are formed by hydrophobicity ionic liquid 1-butyl 3-methyl imidazole six fluoride phosphate ([BMIM]PF₆) as electrolyte using anodization, which indicated that the hydrophilicity or hydrophobicity of ionic liquid plays a vital role in preparing TiO₂ NTs. These studies have shown that ionic liquid acts as a solvent, template, stabilizer and structure guiding agent during the synthesis process, which play an important role in the formation of materials^[22].

Herein, we demonstrated a simple anodization method to synthesize N-doped TiO₂ NT arrays in electrolytes composed of HF, water and [BMIM]BF₄(H₂O/HF/[BMIM]BF₄). These N-doped TiO₂ NT arrays showed superior photocatalytic activity. Furthermore, the influences of [BMIM]BF₄ on their morphologies and structures were also studied.

1 Experiments

Ti sheet, purity > 99.5%, had 0.40 mm thickness. Pt wire, purity > 99.99%, had 0.20 mm diameter. All chemical reagents were of analytical reagent grade quality and purchased from Kermel Chemical Ltd. The ionic liquid, [BMIM]BF₄, was synthesized as described in previous reports^[23,24], the structure of which is shown in Fig.1. Ti sheets were polished with metallographic abrasive paper and washed with abluent and further deionized water, acetone, isopropanol, and methanol in turn by ultrasonic. At last, Ti sheets were rinsed with deionized water and dried in atmosphere.

The self-organized and well-aligned TiO₂ NT arrays were prepared by anodization process. A rectangle Ti sheet (20 mm × 15 mm) was used as the anode and Pt wire as a cathode and the distance between the two electrodes was 2.5 cm in the electrolytes composed of 0.5 wt% HF. By potentiostatic anodization at 20 V for 3 h at room temperature, noncrystal TiO₂ NT arrays were obtained. The preparation method of N-doped TiO₂ NT arrays was consistent with the foregoing preparation method of TiO₂ NT arrays, but [BMIM]BF₄ was added as nitrogen source to electrolytes composed of 0.5 wt% HF. After then, all the samples were rinsed by deionized water and dried in air. As the last step, the samples were calcined directly at 450 °C with a heating rate of 20 °C min⁻¹ for 2 h, and then cooled down in furnace.

The surface morphologies of the samples were characterized with a scanning electron microscope (SEM) (S-4800, Hitachi,

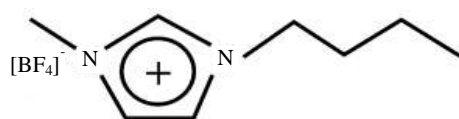


Fig.1 Chemical structure of the ionic liquid used in the present work: [BMIM]BF₄ (1-butyl-3-methylimidazolium tetrafluoroborate)

Japan). The crystalline structures of the samples were examined by a X-ray diffractometer (XRD) (D8 Advance, Bruker, Cu K α radiation, 35 kV, $\lambda=0.15418$ nm). X-ray photoelectron spectroscopy (XPS) (AXIS-ULTRA DLD, Shimadzu) measurements were conducted with Al K α as the exciting source ($h\nu=1486.6$ eV) to get the information on chemical binding energy of the samples. The structures of the samples were characterized with Fourier translation infrared spectroscopy (FT-IR) (Spectrum One, Perkin Elmer). The UV-Vis diffuse reflectance spectra (DRS) of the samples were measured by a diffuse reflectance accessory of UV-Vis spectrophotometry (Lambda950, Perkin Elmer).

The photocatalytic activities of the TiO₂ NT arrays and N-doped TiO₂ NT arrays were measured by the degradation of methylene blue (MB). The samples (20 mm × 15 mm) were entirely immersed into 15 mL MB (10 mg/L). The spherical xenon lamp (150 W) was used as the light source and irradiated perpendicularly to the surfaces of the samples. The distance between the lamp and the sample was 10 cm. The changes of MB concentration were measured by UV-Vis spectrophotometer (T6, Puxi, Beijing) at 664 nm every 20 min.

2 Results and Discussion

2.1 Morphologies of nanotube arrays

Fig.2 shows the SEM images of calcined TiO₂ NT arrays and N-doped TiO₂ NT arrays. After anodization for 3 h, well-aligned nanotube arrays are prepared on Ti sheets. Fig.2a is the top view of calcined TiO₂ NT arrays prepared in 0.5wt% HF solution. It shows that the diameter of nanotubes is 100~110 nm on average. Fig.2b~2d are the SEM images of N-doped TiO₂ NT arrays prepared in 0.5 wt% HF solution containing 0.3 vol%, 0.4 vol% and 0.5 vol% [BMIM]BF₄, respectively. The highly ordered nanotube arrays of TiO₂ NT arrays and N-doped TiO₂ NT arrays have been well prepared on Ti substrates. However, from Fig.2a and Fig.2b we can see that the diameter of N-doped nanotube is 120~130 nm on average which is larger than that of the undoped TiO₂ nanotube, and the surface morphologies of N-doped TiO₂ NT arrays are more uniform than the undoped TiO₂ NT arrays. Because the ionic liquid ([BMIM]BF₄) not only acts as a nitrogen source, solvent, template agent, but also as a structure guiding agent to synthesize inorganic nanomaterial^[18,19,22]. Fig.2c and Fig.2d are the SEM images of N-doped TiO₂ NT arrays prepared in 0.5 wt% HF solution containing 0.4 vol% and 0.5 vol% [BMIM]BF₄, respectively. It is revealed that the diameters of nanotubes are much larger and the walls collapse. Because the BF₄⁻ of [BMIM]BF₄ affords F to synthesize the nanotube structure, the excess [BMIM]BF₄ makes the wall collapse^[20,22].

2.2 XRD analysis

Fig.3 reveals the XRD patterns of TiO₂ NT arrays calcined at 450 °C and N-doped TiO₂ NT arrays prepared in 0.5 wt%

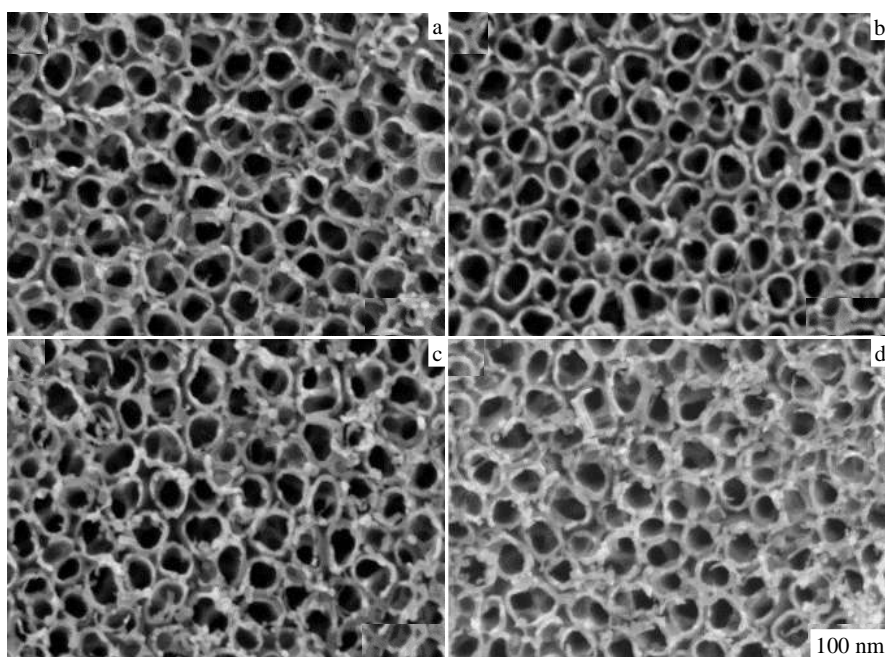


Fig.2 SEM images of TiO₂ NT arrays (a), N-doped TiO₂ NT arrays prepared in 0.5 wt% HF solution containing 0.3 vol% [BMIM]BF₄ (b), containing 0.4 vol% [BMIM]BF₄ (c), and containing 0.5 vol% [BMIM]BF₄ (d)

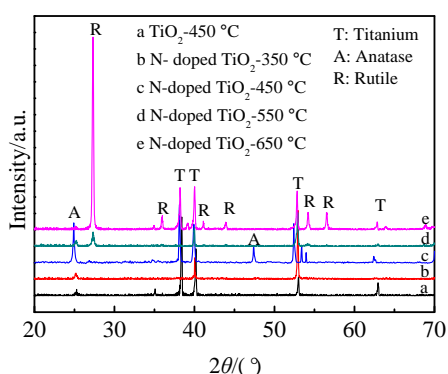


Fig.3 XRD patterns of TiO₂ and N-doped TiO₂ nanotube arrays calcined at different temperatures

HF solution containing 0.3 vol% [BMIM]BF₄ calcined at different temperatures. The TiO₂ is amorphous before calcining. After calcining, crystalline phase of TiO₂ is formed. Anatase phase is the main style in both undoped TiO₂ and N-doped TiO₂, when calcined at 450 °C. Rutile phase in N-doped TiO₂ appears when calcination temperature is increased to 550 °C and it is dominant when calcination temperature is 650 °C. Compared with the XRD patterns, the peak intensity of anatase phase in N-doped TiO₂ is stronger than that in undoped TiO₂ when calcined at 450 °C.

2.3 XPS analysis

The elemental composition and electronic state of N-doped TiO₂ NT arrays prepared in 0.5 wt% HF solution containing 0.3 vol% [BMIM]BF₄ were characterized by XPS (Fig.4).

Fig.4a clearly shows the surface compositions of the N-doped TiO₂ NT arrays are elements Ti, O, N and C, which indicate that nitrogen element is introduced into nanotube. The N 1s peak is broad and asymmetric, which can be fitted by three peaks in Fig.4b. The first peak is at 396.8 eV, attributed to N-Ti linkage^[25,26], and the second peak is at 399.6 eV, attributed to N-Ti-O linkage^[25,27], which indicates the nitrogen atoms replace oxygen atoms in the TiO₂ lattice. The third peak is at 401.0 eV, attributed to Ti-O-N linkage^[28-30]. Nitrogen replaces a part of lattice oxygen of TiO₂, so that the binding energies of titanium and oxygen decrease, resulting in more easy separation of titanium and oxygen and forming of oxygen vacancies. The existence of oxygen vacancies is good for the photocatalytic activity^[31-33]. As shown in Fig.4c, the O 2p peak can be fitted by three peaks. The first peak is at 529.7 eV, attributed to Ti-O linkage, and the second peak is at 531.0 eV, attributed to the •OH adsorbing on the surface of TiO₂ nanotube^[29]. The existence of •OH can improve the photocatalytic activity. The third peak is at 531.9 eV, attributed to Ti-O-N linkage^[28], which are consistent with the analysis of N 1s peak. The Ti 2p peak can be fitted by two peaks at 458.4 and 464.2 eV, corresponding to the two peaks of Ti 2p_{3/2} and Ti 2p_{1/2}, attributed to the Ti in TiO₂ which is Ti⁴⁺ in Fig.4d.

2.4 FT-IR analysis

Fig.5 is the FT-IR spectrum of N-doped TiO₂ NT arrays prepared in 0.5 wt% HF solution containing 0.3 vol% [BMIM]BF₄. As shown in Fig.5, the absorption bands at 3203 cm⁻¹ and 3048 cm⁻¹ are the stretching vibration of unsatura-

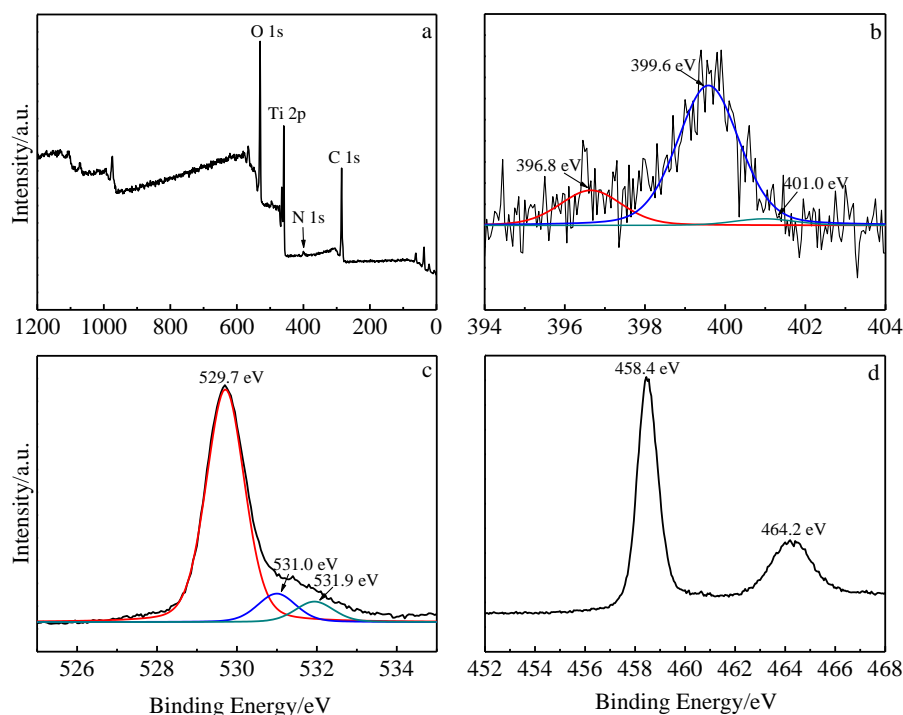


Fig.4 XPS spectra of N-doped TiO₂ NT arrays: (a) survey spectrum, (b) N 1s spectrum, (c) O 1s spectrum, and (d) Ti 2p spectrum

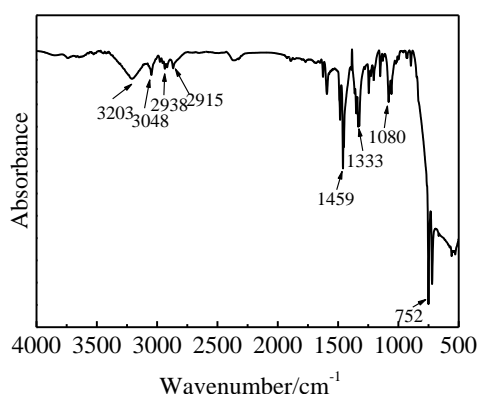


Fig.5 FT-IR spectrum of N-doped TiO₂ NT arrays

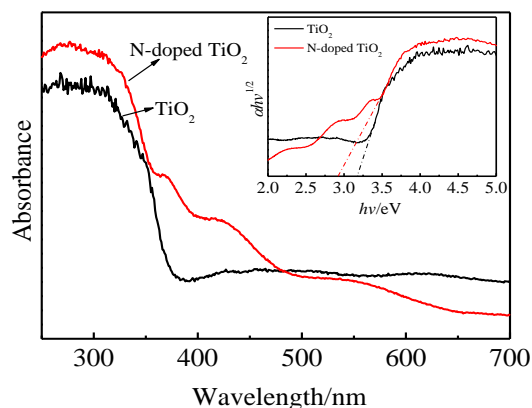


Fig.6 DRS spectra of TiO₂ and N-doped TiO₂ NT arrays

tion C-H bonds belonging to imidazole; at 2938 and 2915 cm^{-1} are the stretching vibration of saturation C-H bonds belonging to $-\text{CH}_3$ and $-\text{CH}_2$, respectively; at 1459 and 1333 cm^{-1} are the stretching vibration of deformation vibration C-H belong to imidazole; at 1080 and 752 cm^{-1} are the stretching vibration belonging to BF_4^- and C-H bonds of butyl, respectively. It shows that there are $[\text{BMIM}]^+$ and BF_4^- in the N-doped TiO₂ NT arrays. It is consistent with the results of the N element which is found in the XPS test. This indicates that the N element in imidazole of ionic liquid ($[\text{BMIM}]\text{BF}_4$) is successfully doped into the TiO₂ lattice. The structure analysis is according to Ref. [18, 29, 30].

2.5 DRS analysis

Fig.6 are the DRS spectra of TiO₂ NT arrays and N-doped

TiO₂ NT arrays prepared in 0.5 wt% HF solution containing 0.3 vol% $[\text{BMIM}]\text{BF}_4$. The inset in Fig.6 is the $(\alpha h\nu)^{1/2}-h\nu$ relation curve (where α is absorption coefficient, h is plank constant, and ν is frequency of ray). Fig.6 shows that the TiO₂ NT arrays in ultraviolet region ($\lambda < 400$ nm) have obvious absorption, but in visible region (400~500 nm) almost no absorption. However, N-doped TiO₂ NT arrays have obvious absorption, both in ultraviolet region ($\lambda < 400$ nm) and in visible region (400~500 nm). From the $(\alpha h\nu)^{1/2}-h\nu$ relation curve, we get the band gaps of TiO₂ NT arrays and N-doped TiO₂ NT arrays are 3.19 eV and 2.92 eV, respectively. This is because the impurity level introduced by N 2p and O 2p orbital hybridization can narrow the band gap, which make the N-doped TiO₂ NT arrays response to visible light stronger than

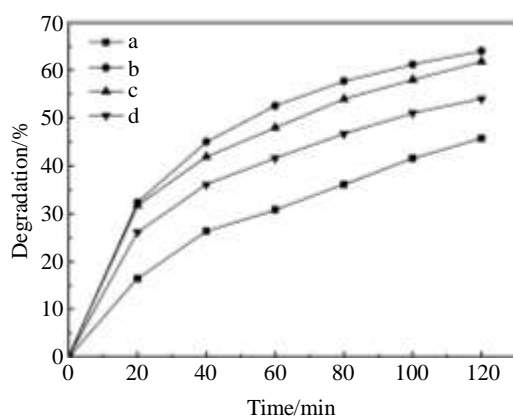


Fig.7 Degradation of MB by TiO₂ NT arrays (a), N-doped TiO₂ NT arrays prepared in 0.5 wt% HF solution containing 0.3 vol% [BMIM]BF₄ (b), containing 0.4 vol% [BMIM]BF₄ (c), and containing 0.5 vol% [BMIM]BF₄ (d)

TiO₂ NT arrays^[31,32].

2.6 Photocatalytic activity

Fig.7 shows the degradation of MB (15 mL, 10 mg/L) under spherical xenon lamp (150 W) by TiO₂ nanotube arrays and N-doped TiO₂ NT arrays prepared in 0.5 wt% HF solution containing 0.3 vol%, 0.4 vol% and 0.5 vol% [BMIM]BF₄. After 2 h, the corresponding degradation data of N-doped TiO₂ NT arrays are 64.02%, 61.82%, and 54.01%, respectively, which are higher than that of TiO₂ NT arrays (45.74%). The results show that the N-doped TiO₂ NT arrays have the higher photocatalytic activity than undoped TiO₂ NT arrays. The enhanced photocatalytic ability could be ascribed to the N doping. During N doping, nitrogen replaces a part of lattice oxygen of TiO₂ and then oxygen vacancies are formed. The existence of oxygen vacancies enhances the response to visible light. At the same time, the 2p orbital of the doped N atoms is significantly interacting with that of O 2p, forming an impurity level to narrow the band gap. Therefore, N-doped TiO₂ NT arrays show higher photocatalytic activity than TiO₂ NT arrays. The results are in good agreement with those of the XPS and DRS investigation.

3 Conclusions

1) N-doped TiO₂ NT arrays can be prepared by anodization in HF solution containing [BMIM]BF₄.

2) The N-doped TiO₂ NT arrays can respond under visible light, and exhibit superior photocatalytic activity under visible light in comparison with undoped TiO₂ NT arrays. It is attributed to N doping which can decrease the band gap and increase oxygen vacancies caused by the formation of O-Ti-N and Ti-O-N linkage.

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离子液体辅助阳极氧化法制备 N 掺杂 TiO₂ 纳米管阵列及其光催化性能研究

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摘 要: 以 HF 水溶液为电解液, 离子液体 (1-丁基-3-甲基咪唑四氟硼酸盐 [BMIM]BF₄) 为 N 源, 采用阳极氧化法制备 N 掺杂 TiO₂ 纳米管阵列。通过扫描电子显微镜 (SEM)、X 射线衍射 (XRD)、X 射线光电子谱 (XPS)、傅里叶变换红外光谱 (FT-IR) 和紫外-可见漫反射光谱 (DRS) 对 N 掺杂 TiO₂ 纳米管阵列的表面形貌、晶型和氮元素的掺杂方式进行分析。以球形氙灯为光源, 亚甲基蓝溶液为目标降解物测试 N 掺杂 TiO₂ 纳米管阵列的光催化活性。结果表明, N 掺杂 TiO₂ 纳米管阵列对亚甲基蓝溶液的降解率明显高于未掺杂的 TiO₂ 纳米管阵列。这是因为 N 掺杂后不仅使 TiO₂ 禁带宽度变窄, 并且 N 掺杂进入 TiO₂ 晶格中形成 O-Ti-N 键和 Ti-O-N 键, 使氧空位数量增加, 从而使其光催化活性提高。

关键词: TiO₂ 纳米管阵列; 离子液体; N 掺杂; 阳极氧化; 光催化

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