Preparation and photocatalytic application of nonmetallic doped TiO_2 films with narrow band gap

Chenglong Sun

Materials Science and Engineering, Ocean University of China, Qingdao, Shandong, 266100, China

sunchenglong@stu.ouc.edu.cn

Abstract. TiO_2 thin film has become a widely used photocatalyst due to its stable chemical properties, suitable edge position, non-toxicity and low cost, and the film structure is conducive to recycling and loading. However, because the band gap of titanium dioxide is relatively wide, visible light is difficult to be utilized, which also limit the utilization of TiO_2. In recent years, non-metallic doping has been proven to be an extraordinarily efficient methodologies to reduce band gap and improve photocatalytic efficiency of TiO_2 films. In this paper, the basic principle of photocatalysis and the principle of reducing band gap by doping inorganic non-metallic elements are briefly introduced, and the preparation methods of N, C and B inorganic non-metallic elements doped TiO_2 films are reviewed, as well as their functions on reducing band gap of TiO_2. Finally, the research status of inorganic non-metallic element doped TiO_2 thin film in photodecomposition of water and organic decomposition in catalytic solution was introduced.

Keywords: titanium dioxide, film, non-metal doping, photocatalysis.

1. Introduction

With the rapid development of today's society, mankind has created countless wealth and achievements by virtue of advanced science and technology, but it also led to environmental destruction and energy shortage. How to obtain clean and cheap energy supply and manage the environment at low cost has become the goal pursued by researchers. Since the discovery of photocatalysis by Fujishima et al. [1]in 1972, it has become the most studied of many methods. With the photocatalytic effect of semiconductor materials optical energy can be utilized to decompose water and produce hydrogen, a kind of clean energy which can partially solve the lack of traditional energy. It can also degrade organic pollutants, reduce heavy metal ions, protect soil and water, and effectively improve the environment.

The most important research of photocatalysis is photocatalyst. Among many photocatalysts, TiO_2 has become the most widely used photocatalyst due to its good band position, which well matches the REDOX potential of H_2O and CO_2, stable chemical properties, strong corrosion resistance, non-toxicity and low cost [2]. However, both crystalline structures of TiO_2 have a wide energy gap [3] (anatase 3.2eV, rutile 3.0eV), which enables TiO_2 to absorb sunlight mainly in the ultraviolet range. However, the proportion of ultraviolet rays in the solar spectrum is only 4-5% [4], which means that a large proportion of sunlight is wasted. Therefore, we hope to reduce the inherent band gap of titanium

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dioxide to increase the absorption rate of sunlight. There are many ways to reduce the band gap, including doping metal atoms (Fe, Cu) and nonmetal atoms (N, C, S, F, etc.) into the TiO_2 lattice [5]. However, metal doping can lead to thermolability and increase carrier capture rate, thus reducing photocatalytic efficiency [6]. In addition, more expensive ion injection facilities are required to synthesis transition metal doped TiO_2 films. Therefore, nonmetals are considered a more feasible approach.

Although powders with larger specific surface area because they can be suspended in liquid may have higher photocatalytic efficiency, nano-powders or ultrafine powders have the disadvantage of being difficult to recover after reaction. Considering the practical value of TiO_2, they are often supported at present, and many TiO_2 applications involve TiO_2 thin films.

This review will focus on the principle of non-metallic doping to narrow band gap, and the preparation of various N, C and B doped TiO_2 films. The photocatalytic application of doped titanium dioxide thin film will also be briefly introduced.

2. Principle of doping

2.1. Principle of Photocatalysis

Photocatalysis takes advantage of electron-hole pairs generated by semiconductors irradiated by light to participate in oxidation-reduction reactions. When light of which the wave length is shorter enough irradiates TiO_2, electrons in its valence band (VB) will be stimulated to conduction band (CB), leaving vacancies called holes in valence band at the same time, thus forming electron-hole pairs. Electrons or holes will be captured by the defect or suspension bond of TiO_2, which makes it difficult to recombine [7]. These electron-hole pairs diffuse to the surface of the film, creating a strong oxidation and reduction potential. Photogenic electrons are easily captured by oxidizing substances to generate superoxide radical $\cdot O^2$-. At the same time, the OH- and H_2O can be oxidized by holes on the surface of TiO_2 to hydroxyl radical ·OH. $\cdot O^2$- and ·OH have strong oxidation capacity, which can almost break the chemical bonds of all kinds of organic matter. Therefore, various organic pollutants can be decomposed into inorganic small molecules, CO_2, H_2O and other substances to achieve the purpose of purification [8].

2.2. Principle of Reducing Band Gap by Doping Non-metallic Atoms

In addition to unstable plate titanium, anatase and rutile are common stable structures of TiO_2. Although the anatase structure has a slightly wider band gap(3.2eV) than rutile(3.0eV), the excited electrons and holes are not easily recombined in anatase, so it has higher photocatalytic activity and is more commonly used as a photocatalyst.

As shown in Fig.1, the energy gap of anatase titanium dioxide between VB and CB is 3.2eV. B, C and N are all second-period elements with small atomic radii and are likely to diffuse to lattice atoms through lattice gaps. According to the band theory, these doped atoms can introduce impurity levels into the original band gap of anatase [9]. Because these impurity levels are in the forbidden band, electrons and holes can be captured by them. Electrons and holes trapped at impurity levels can also be excited when photons with lower energy are illuminated. In this way, the band gap of anatase titanium dioxide is recognized to be narrowed.

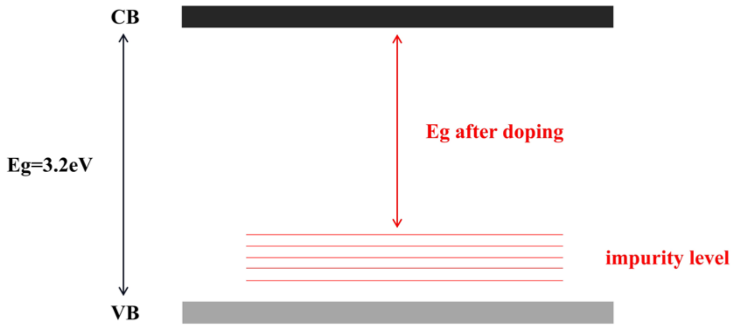

Figure 1. Band structure of anatase(Eg=3.2eV) doped with inorganic nonmetals.

3. Synthesis of films

3.1. N Doping

Since N is very close to the position of O element and has a similar radius with O atom, it is very easy to form substituted atoms [10,11]. Therefore, N-doping is the most studied non-metallic doped atom at present. According to Xu et al. [12], the energy gap of N doped TiO_2(Eg=2.33eV) was slightly smaller than that of original TiO_2(Eg=2.47eV), and three N 2p bands were located near the Fermi level, higher than the maximum VB of anatase. The isolated 2p level introduced by N atom should be responsible for the enhanced photocatalytic ability of anatase. Many methods have been taken to prepare N-doped TiO_2 thin films. Sun et al. [13] deposited N-doped TiO_2 thin films on glass and 316L stainless steel using N_2 as nitrogen source by double-pulse DC magnetron sputtering and annealed them to obtain a minimum band gap of 2.55eV. The results show that the TiON 1-3 films have a hybrid polycrystalline structure of anatase and rutile. Cheng et al. [14] prepared N-doped TiO_2 thin films by atomic layer deposition using ammonia as the source of nitrogen and ammonia, steam mixture of TiCl4 and water as reactants. The experiment shows that the photocurrent response of N-doped TiO_2 thin film has expanded to the visible light range, indicating that the band gap has been reduced, and it is concluded that the optimal doping concentration of N-doped TiO_2 thin film is between 0.7 and 1.2%. Shen et al. [15] doped N ions directly into anatase TiO_2 thin films by pulsed laser deposition using low energy ion implantation. The experimental results show that the nitrogen doped by this method is interspace rather than substitution mainly due to the very low implantation energy. Moreover, irradiated with visible light, N-doped TiO_2 film shows high photocatalytic activity by decomposition of methylene blue (MB) solution, and its visible photocatalytic efficiency increases with the increase of implanted nitrogen content.

3.2. C Doping

Irie et al. [16] prepared C-doped TiO_2 powder in 2003, and proved that C-doped TiO_2 powder could decompose isopropyl amine into acetone and CO_2 under visible light. It was proved that C atoms were located at the occupancy site of O and can highly decrease the width of the band gap, but the mass fraction of carbon doping in TiO_2 using the oxidizing method was relatively low, with merely 0.32%. Since then, many preparation methods of high C doped TiO_2 thin films have been discovered. Wu et al. [17] successfully prepared TiO_2 films with high percentage content of C doping (x=0.24) through a two-step method. The band gap is calculated to be 2.77eV, which is obviously reduced. Nakano et al. [18] synthesized C-permeable TiO_2 films by oxidative annealing of sputtering TiC films, and characterized the films by deep level optical spectroscopy (DLOS). In this research, it was showed that the band gap of 2.34eV, which plays an important role in affecting visible light sensitivity. In addition, Mai et al. [19] used traditional sol-gel method to successfully prepared C-doped TiO_2 films. In this study, XPS was used to prove that C delayed the structural transition from anatase to rutile by forming O-Ti-C bond at the interface of anatase TiO_2. In addition, it was found that the band gap gradually

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redshifted with the increase of C dopant concentration from 0.1-0.3%, reaching a minimum of 2.87eV (x=0.3%). In addition to C doping, TiO_2 and GO nanosheets were also prepared by some studies. The band gap of TiO_2 and GO nanosheets (1.40eV) was also significantly reduced compared with that of original TiO_2 samples(3.42eV) [20].

3.3. B Doping

Not all studies support that B doped TiO_2 photocatalyst can cause band gap red shift. Chen et al. [21] found that the absorption limitation of B-doped titanium dioxide samples moved significantly to the short-wave direction and the band gap increased. As for the improve of photocatalytic ability, Chen attributed it to the quantization effect of nanoparticles, that is, the increase of band gap can improve the REDOX capacity of TiO_2, thus improving the photocatalytic activity. However, a series of studies have found that B doping can narrow the band gap. Zhao et al. [22] prepared co-doped TiO_2 photocatalyst by combining B doped TiO_2 and Ni2O3 using improved SOL-gel method, and used it to degrade chlorophenol. The results show that both co-doping and single B-doping exhibit certain catalytic activity in the visible region. Kubelka-Munk function calculation indicates that the energy gap of B-doped TiO_2 (Eg = 2.93eV) is 0.25eV lower than that of pure TiO_2 (Eg = 3.18eV). Lu et al. [23] first synthesized b-doped TiO_2 nanotube array film as electrode by anodic oxidation method. Diffuse reflectance spectroscopy (DRS) analysis of B - doped TiO_2 electrode was carried out. The research found that the energy gap between CB and VB in pure TiO_2 (3.34eV) decreased significantly (3.10eV) with the addition of B.

In addition to N, C and B doping, there are currently P, F, S and other single non-metallic elements doping, as well as multiple non-metallic or non-metallic co-doping with metal, which will not be discussed here.

4. Applications of Nonmetal-Doped TiO_2

4.1. Water Splitting

Hydrogen is an excellent clean renewable energy source that can be efficiently converted to and from electrical energy. Hydrogen has a series of advantages such as lightest weight, good thermal conductivity, abundant reserves and environmental protection. Hydrogen can be obtained by photocatalytic decomposition of water. The photocatalyst that can be used for photodecomposition of water must meet two conditions: 1) The band gap must be higher than the energy of water decomposition to ensure that enough energy can be generated to decompose water; 2) The potential of the bottom of CB is higher than the reduction electrode potential of H_2O (0 V vs. NHE), and the potential of the top of VB is lower than the oxidation electrode potential of H_2O (1.23V vs. NHE) [2]. Islam et al. [24] successfully and rapidly prepared N-doped mesoporous TiO_2 thin films. In this study, photocatalytic activity induced by ultraviolet and visible light was tested. N-doped TiO_2 films show stronger photocatalytic activity than original TiO_2 films in both UV and visible light. Compared with powder, thin film is easier to be used as a load to prepare larger solar catalytic water decomposition system for hydrogen production.

4.2. Sewage Treatment

Many industrial wastewaters can not be directly discharged into the water body, because the composition of these industrial wastewater is relatively complex, industrial wastewater often contains different concentrations and different components of chemical substances, many chemicals even have high economic value, at the same time has a certain toxicity. In order to protect the water body pollution of the environment in our country, it is necessary to recycle the ingredients in these water bodies, must according to the purification of emissions of industrial waste water effectively, the photocatalytic technology, for the use of the material circulation in the industrial wastewater, on the one hand can reduce environmental pollution, on the other hand can guarantee material recycling. Hu et al. [25] synthesized core-shell TiO_2-C composite films with three-dimensional network microstructure by hydrothermal method and annealing, and measured the photodecomposition rate of MB catalyzed by TiO_2 nanoparticles, TiO_2 clad with TiO_2-C composite materials and TiO_2-C@TiO_2-C composite films in the experiment. The rate constants of TiO_2 nanoparticles, TiO_2-C@TiO_2 composite materials and TiO_2-C core-shell composite films increased successively. Shen et al. [15] synthesized N-doped TiO_2 thin films by ion implantation with lower energy and showed visible photocatalytic activity when decomposing MB. For original TiO_2, visible light could not induce any photocatalytic activity. In addition, after 12 h of visible light irradiation at 405 nm, TiO_2 film with 3.4% nitrogen concentration could catalyze the decomposition of 51% MB in aqueous solution, proving that N-TiO_2 film had photocatalytic decomposition ability of MB under visible light.

5. Conclusion

TiO_2 thin films are widely used as photocatalysts due to their excellent properties. In order to overcome the difficulty of using UV light caused by broadband gap, non-metallic doping is used to narrow the band gap. In this paper, the preparation methods of typical TiO_2 films doped with N, C and B elements, their band gap narrowing performance and some experimentally proven photocatalytic applications are introduced. It can be seen that non-metallic doping has an obvious effect on band gap narrowing, which makes TiO_2 thin film transfer from wide band gap semiconductor to narrow band gap semiconductor. However, although non-metallic doping significantly enhances the photoactivity of TiO_2 visible light, titanium dioxide still has various problems in visible light absorption and separation of photon-generated carriers in practical photocatalytic applications, which need to be further improved. In the future, it is necessary to conduct more in-depth research on the co-doping mechanism and carry out research on the preparation of composite materials with noble metal doped semiconductors.

References

[1] Fujishima, A., Honda, K., 1972. Electrochemical Photolysis of Water at a Semiconductor Electrode. Nature 238, 37–38.. doi:10.1038/238037a0
[2] Islam, S., Nagpure, S., Kim, D., Rankin, S., 2017. Synthesis and Catalytic Applications of Non-Metal Doped Mesoporous Titania. Inorganics 5, 15.. doi:10.3390/inorganics5010015
[3] Landmann, M., Köhler, T., Köppen, S., Rauls, E., Frauenheim, T., Schmidt, W.G., 2012. Fingerprints of order and disorder in the electronic and optical properties of crystalline and amorphous TiO_2. Physical Review B 86.. doi:10.1103/physrevb.86.064201
[4] Pelaez, M., Nolan, N.T., Pillai, S.C., Seery, M.K., Falaras, P., Kontos, A.G., Dunlop, P.S.M., Hamilton, J.W.J., Byrne, J.A., O'Shea, K., Entezari, M.H., Dionysiou, D.D., 2012. A review on the visible light active titanium dioxide photocatalysts for environmental applications. Applied Catalysis B: Environmental 125, 331–349.. doi:10.1016/j.apcatb.2012.05.036
[5] Ismail, A.A., Bahnemann, D.W., 2011. Mesoporous titania photocatalysts: preparation, characterization and reaction mechanisms. Journal of Materials Chemistry 21, 11686.. doi:10.1039/c1jm10407a
[6] Cong, Y., Zhang, J., Chen, F., Anpo, M., 2007. Synthesis and Characterization of Nitrogen-Doped TiO_2 Nanophotocatalyst with High Visible Light Activity. The Journal of Physical Chemistry C 111, 6976–6982.. doi:10.1021/jp0685030
[7] Wang, Z., Liu, Y., Huang, B., Dai, Y., Lou, Z., Wang, G., Zhang, X., Qin, X., 2014. Progress on extending the light absorption spectra of photocatalysts. Physical Chemistry Chemical Physics 16, 2758.. doi:10.1039/c3cp53817f
[8] Hoffmann, M.R., Martin, S.T., Choi, W., Bahnemann, D.W., 1995. Environmental Applications of Semiconductor Photocatalysis. Chemical Reviews 95, 69–96.. doi:10.1021/cr00033a004
[9] Ansari, S.A., Khan, M.M., Ansari, M.O., Cho, M.H., 2016. Nitrogen-doped titanium dioxide (N-doped TiO_2) for visible light photocatalysis. New Journal of Chemistry 40, 3000–3009.. doi:10.1039/c5nj03478g
[10] Khan, M.M., Adil, S.F., Al-Mayouf, A., 2015. Metal oxides as photocatalysts. Journal of Saudi

Chemical Society 19, 462–464.. doi:10.1016/j.jscs.2015.04.003

[11] Dunnill, C.W., Parkin, I.P., 2011. Nitrogen-doped TiO2thin films: photocatalytic applications for healthcare environments. Dalton Transactions 40, 1635–1640.. doi:10.1039/c0dt00494d

[12] Xu, T.-H., Song, C.-L., Liu, Y., Han, G.-R., 2006. Band structures of TiO_2 doped with N, C and B. Journal of Zhejiang University-Science B 7, 299–303.. doi:10.1631/jzus.2006.b0299

[13] Sun, Z., Pichugin, V.F., Evdokimov, K.E., Konishchev, M.E., Syrtanov, M.S., Kudiiarov, V.N., Li, K., Tverdokhlebov, S.I., 2020. Effect of nitrogen-doping and post annealing on wettability and band gap energy of TiO_2 thin film. Applied Surface Science 500, 144048.. doi:10.1016/j.apsusc.2019.144048

[14] Cheng, H.-E., Lee, W.-J., Hsu, C.-M., Hon, M.-H., Huang, C.-L., 2008. Visible Light Activity of Nitrogen-Doped TiO[sub 2] Thin Films Grown by Atomic Layer Deposition. Electrochemical and Solid-State Letters 11, D81.. doi:10.1149/1.2968951

[15] Shen, H., Mi, L., Xu, P., Shen, W., Wang, P.-N., 2007. Visible-light photocatalysis of nitrogen-doped TiO_2 nanoparticulate films prepared by low-energy ion implantation. Applied Surface Science 253, 7024–7028.. doi:10.1016/j.apsusc.2007.02.023

[16] Irie H, Watanabe Y, Hashimoto K. Carbon-doped anatase TiO_2 powders as a visible-light sensitive photocatalyst[J]. Chemistry Letters, 2003, 32(8): 772-773..doi:10.1246/cl.2003.772

[17] Wu, J., Jiang, X., Zhang, Y., Fu, Q., Pan, C., 2018. Preparation of high-concentration substitutional carbon-doped TiO_2 film via a two-step method for high-performance photocatalysis. RSC Advances 8, 36691–36696.. doi:10.1039/c8ra07082b

[18] Nakano, Y., Morikawa, T., Ohwaki, T., Taga, Y., 2005. Electrical characterization of band gap states in C-doped TiO_2 films. Applied Physics Letters 87, 052111.. doi:10.1063/1.2008376

[19] Mai L, Huang C, Wang D, et al. Effect of C doping on the structural and optical properties of sol–gel TiO_2 thin films[J]. Applied Surface Science, 2009, 255(22): 9285-9289..doi:10.1016/j.apsusc.2009.07.027

[20] Timoumi, A., Alamri, S.N., Alamri, H., 2018. The development of TiO_2-graphene oxide nano composite thin films for solar cells. Results in Physics 11, 46–51.. doi:10.1016/j.rinp.2018.06.017

[21] Chen, D., Yang, D., Wang, Q., Jiang, Z., 2006. Effects of Boron Doping on Photocatalytic Activity and Microstructure of Titanium Dioxide Nanoparticles. Industrial & Engineering Chemistry Research 45, 4110–4116.. doi:10.1021/ie0600902

[22] Zhao, W., Ma, W., Chen, C., Zhao, J., Shuai, Z., 2004. Efficient Degradation of Toxic Organic Pollutants with Ni2O3/TiO_2-xBx under Visible Irradiation. Journal of the American Chemical Society 126, 4782–4783.. doi:10.1021/ja0396753

[23] Lu, N., Quan, X., Li, J., Chen, S., Yu, H., Chen, G., 2007. Fabrication of Boron-Doped TiO_2 Nanotube Array Electrode and Investigation of Its Photoelectrochemical Capability. The Journal of Physical Chemistry C 111, 11836–11842.. doi:10.1021/jp071359d

[24] Islam, S.Z., Reed, A., Wanninayake, N., Kim, D.Y., Rankin, S.E., 2016. Remarkable Enhancement of Photocatalytic Water Oxidation in N2/Ar Plasma Treated, Mesoporous TiO_2 Films. The Journal of Physical Chemistry C 120, 14069–14081.. doi:10.1021/acs.jpcc.6b02622

[25] Hu L, Zhang Y, Zhang S, et al. Facile fabrication of transparent TiO_2-C@ TiO_2-C free-standing film for visible-light photocatalytic application[J]. Solid State Sciences, 2017, 64:1-6..doi:10.1016/j.solidstatesciences.2016.12.003