Rare Metal Materials and Engineering
Volume 49, Issue 7, July 2020
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Rare Metal Materials and Engineering, 2020, 49(7): 2281-2288

ARTICLE

A Novel Route for Preparation of Magnéli Titanium Suboxides by Aluminothermic Reduction and Their Photocatalytic Activity Under Visible Light

Li Jun, Wu Enhui, Hou Jing, Huang Ping, Jiang Yan, Xu Zhong, Liu Qianshu

International Research Institute of Vanadium and Titanium, Panzhihua University, Panzhihua 617000, China

Abstract: Magnéli-phases titanium suboxides were prepared by an aluminum reduction-hydrochloric acid leaching route. The resulting sample was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-visible diffuse reflectance spectroscopy (UV-Vis DRS) and X-ray photoelectron spectroscopy (XPS). The results show that Magnéli phase titanium suboxide with Ti_4O_7 as the mother phase could be prepared with the calcination temperature of 950 °C, roasting time of 20 min and the amount of aluminum 0.2. The as-prepared Magnéli-phase titanium suboxides samples with the diameters of 400~600 nm. The surface of Magnéli-phase titanium suboxides forms of oxygen vacancies, and thus the sample shows strong UV and visible-light absorption property. The degradation efficiency of 37%, 43%, and 62% is achieved for the as-prepared Magnéli-phase titanium suboxides samples with 950 °C calcination for 20, 25 and 35 min, respectively, after visible light irradiation for 130 min.

Key words: aluminothermic reduction; Magnéli-phase; photocatalytic degradation

Titanium dioxide (TiO_2) has attracted extensive interest in the fields of photocatalysis, solar cells and solar thermal collectors because of its fascinating features such as low environmental burden, biocompatibility, low cost, chemical stability, excellent electronic, optical properties, high specific surface areas, tunable mesostructures and pore sizes[1-6]. However, its band gap of more than 3.0 eV means that TiO_2 can absorb only the UV part of the solar spectrum, which accounts for about 5% of the solar radiation on the Earth.

Many investigations have attempted to enhance visible-light absorption by band structure engineering.TiO_2 is doped by different impurities including metal elements such as Al, Cr, V[7]; nonmetallic elements such as C[8-10], N[11,12], S[13,14] and many others. Although the ability to absorb visible light of doped titanium dioxide is enhanced, this absorption enhancement is not very effective for visible-light photocatalysis. Hence, the current photocatalytic activity of TiO_2 remains insufficient. Recently, TiO_2-based Z-scheme photocatalysts have attracted considerable attention because of the low recombination rate of their photogenerated electron-hole pairs and their high photocatalytic efficiency[15]. Z-scheme photocatalysts such as TiO_2/g-C_3N_4[16,17], ZnO/TiO_2[18], Ag_2O/TiO_2[19] were intensively studied, which exhibited good photocatalytic activity.

The Magnéli phases of titanium oxides comprise a series of nonstoichiometric compounds with a generic formula Ti_nO_{2n-1}, where n is a number ranging from 4 to 10[20,21]. Compared with TiO_2, Ti_nO_{2n-1} phases have superior performance in many fields. For example, the mixture of Ti_nO_{2n-1} with n=4~10 have been confirmed to have great visible light response due to the narrower bandgap compared with anatase or rutile, which is very suitable for visible light photocatalysis. The Magnéli phases of titanium oxides has excellent photocatalytic properities of visible light such as carbon-coated Magnéli phases were prepared

Received date: July 25, 2019
Foundation item: Science and Technology Support Program of Sichuan (2017JY0117); Applied Technology Research and Development Fund of Panzhihua City (2017CY-G-15)
Corresponding author: Li Jun, Ph. D., Assistant Researcher, Panzhihua University, Panzhihua 617000, P. R. China, E-mail: lidejun163@126.com

by Masahiro Toyoda and the materials were reported to have excellent photocatalytic activity under visible light[22-24]. Therefore, numerous methods of producing Magnéli-phase titanium suboxides were developed. These materials could be prepared by reduction of TiO_2 with H_2[25], NH_3[26], C[27], Si[28], PVA[29], Ti[30]. Most of the production methods are processing at high temperature in reductive gases or inert gases, and the reaction needs a long time, especially for the solid-phase reaction of TiO_2 and Ti, which increase the cost of the production by leaps and bounds.

In the present paper, Magnéli phases titanium oxides powders were synthesized by an aluminothermic reduction method, which is low-cost, operated easily and applicable for industrial production. In this work, the influence of calcination temperature, roasting time and the amount of aluminum was studied, and the formation and the characterization of the products were identified. The photocatalytic activity of the recently synthesized Magnéli phases titanium oxides powders was also investigated by methylene blue (MB) dye under the visible light irradiation.

1 Experiment

Anatase-type TiO_2 (typically 0.4~0.6 μm in diameter) were purchased from Sichuan Province Excellence Vanadium and Titanium Co., Ltd. Aluminum powder (99.3% purity, 6 μm Particle size) were purchased from Jiangsu Tian Yuan Metal Powder Co., Ltd. XRD pattern and SEM image of TiO_2 power are shown in Fig.1.

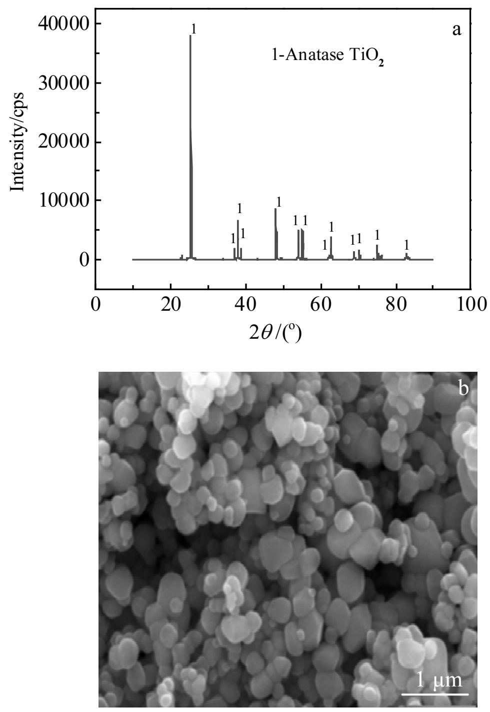

Fig.1 XRD pattern (a) and SEM image (b) of titanium dioxide powder

Preparation process of Magnéli phase titanium suboxides is shown in Fig.2. The anatase TiO_2 powder mixed with Al powder was placed in an alumina crucible which was roasted in a high temperature resistance furnace. We had attempted all the reaction conditions, such as reaction temperature, reaction time and the amount of Al. Reaction time of 10~60 min were employed, while the ratio of Al:TiO_2 was varied corresponding to the reaction equation with 10%~60%, and the reaction temperatures were changed between 800 °C and 950 °C.

In order to remove Al and Al_2O_3 from the as-prepared Magnéli phases titanium oxides powders, a hydrochloric acid pickling method was used. The prepared sample was mixed with hydrochloric acid in a beaker at a stirring rate of 100 r/min, and it was filtered using a vacuum suction funnel after the reaction was completed. The concentration of hydrochloric acid was 4 mol/L and the liquid-solid ratio was 1:25.

Photocatalytic activity of the synthesized Magnéli phases titanium oxides powders was analyzed by the degradation of methylene blue (MB) under a 500 W Xenon lamp equipped with a cutoff filter (λ>420 nm). A quantity of 5 mg of photocatalyst was poised in a 150 mL aqueous MB dye solution (2 mol/L). Previous to the light, the suspensions were ultra-sonicated for 20 min under dark condition for 1 h to make sure that the MB dye would be adsorbed to saturation level on the surface of catalysts. The photocatalytic reaction was carried out at pH=7.0.

Powder X-ray diffraction (XRD) profiles were obtained using a D/max22500PC of Japanese Science and Technology with Cu Kα (λ=0.154 nm) radiation as the incident beam. Transmission electron microscopy (TEM) was performed on a Hitachi H-9000 instrument operating at 300 kV. Scanning electron microscopy (SEM) was performed on JEOL JSM-6060S and JSM-6700F instruments. XPS profiles were obtained by Phi-5000 versaprobe of America.

2 Results and Discussion

2.1 Phase change of samples under different technological conditions

Fixed conditions was Al/TiO_2=0.6 and sintering time was 20 min. Fig.3 shows the XRD pattern of the prepared sample by aluminothermic reduction under 800, 850, 900, 950 °C.

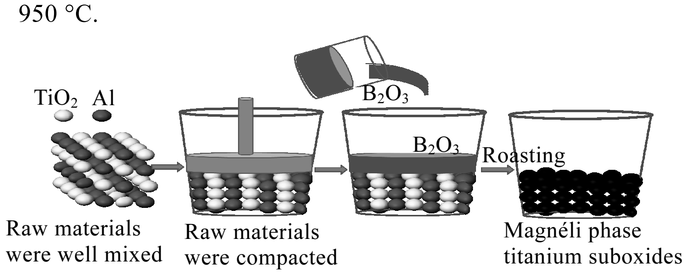

Fig.2 Preparation process of Magnéli phase titanium suboxides

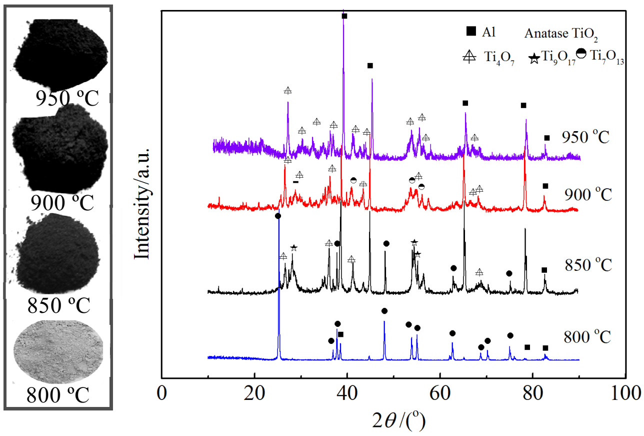

Fig.3 XRD patterns of the black product at different reaction temperatures

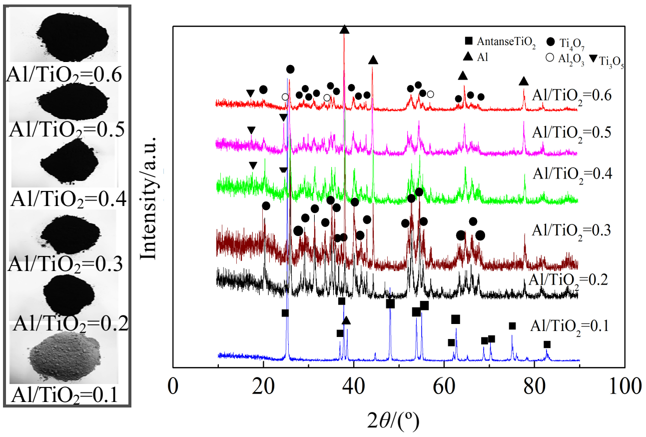

Fig.5 XRD patterns of the black product with different Al contents

As shown in Fig.3, the mother phase was anatase TiO_2 when the samples were sintered below 800 °C. The mother phase transformed to Ti_4O_7 and Ti_9O_{17} when the samples were sintered at 850 °C. The mother phase turned to be Ti_4O_7 completely when the samples were sintered at 950 °C.

Fig.4 shows the XRD pattern of the prepared sample by aluminothermic reduction under different sintering time. As shown in Fig.4, the mother phase was anatase TiO_2 when the samples were sintered below 10 min. The mother phase transformed to Ti_4O_7 when the samples were sintered at 20~50 min. The Ti_3O_5 and Ti_2O_3 started appearing when the samples were sintered at 60 min.

Fig.5 shows the XRD pattern of the prepared sample by aluminothermic reduction under different amounts of aluminum. As shown in Fig.5, the mother phase was anatase TiO_2 when the samples were sintered below Al/TiO_2=0.1.

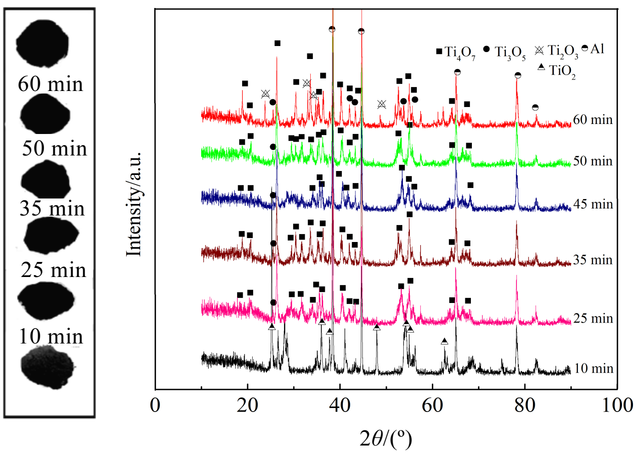

Fig.4 XRD patterns of the black product under different sintering time

The mother phase transformed to Ti_4O_7 when the samples were sintered below $Al/TiO_2 > 0.2$.

Combined with the phase analysis of the sample under different process conditions as shown in Fig.1, Fig.2 and Fig.3, we could obtain the following conclusion that the mother phase is Ti_4O_7 of Magnéli phase titanium oxide prepared at the calcination temperature of 950 °C, when the roasting time is 20 min and the amount of aluminum is 0.2.

The Magnéli-phase sample contains excess Al as shown in Fig.5. Magnéli phase titanium suboxides did not react with sulfuric acid, nitric acid, hydrochloric acid and caustic soda because it has excellent resistance to corrosion candle at room temperature, as shown in Table 1. But the Al and Al_2O_3 could be effectively removed when the sample was dissolved in hydrochloric acid and filtered. The main reaction equations are expressed as Eq.(1) and Eq.(2):

$$2Al(s) + 6HCl(l) = 2AlCl_3(l) + 3H_2(g) \tag{1}$$

$$Al_2O_3(s) + 6HCl(l) = 2AlCl_3(l) + 3H_2O(l) \tag{2}$$

Pure Magnéli-phase titanium suboxides (Ti_4O_7) could be obtained after the sample dissolved in hydrochloric acid and filtered, such as illustrated in Fig.6.

2.2 XPS spectra of as-prepared Magnéli phase titanium suboxides

X-ray photoelectron spectroscopy (XPS) was employed to further investigate the transformation of surface chemical bonding and detect the electronic valence band position of the titanium suboxides. Fig.7 shows the Ti 2p and O 1s core level XPS spectra of the anatase TiO_2. Fig.7b shows that

Table 1 Mass loss of Magnéli phase titanium suboxides (%)

Sample	Acid	150 h	350 h
Ti_4O_7	H_2SO_4	0	0
Ti_4O_7	HCl	0	0
Ti_4O_7	HF	0.017	0.29
Ti_4O_7	HF/HNO_3	0.56	12.7

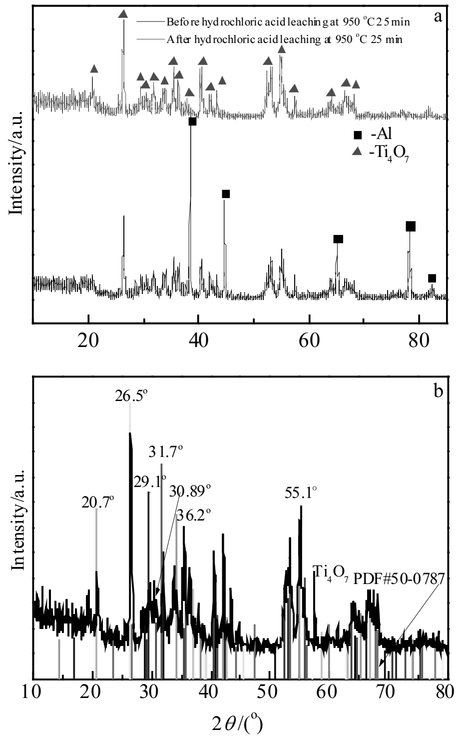

Fig.6 XRD patterns of the black product (a) and Ti_4O_7 PDF#50-0787(b)

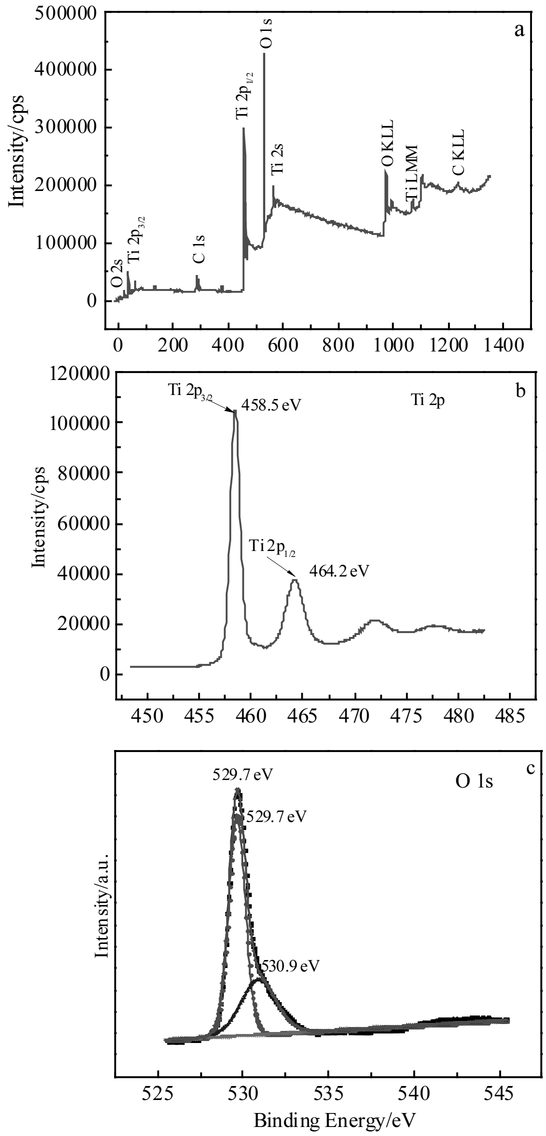

Fig.7 Full spectrum (a), Ti 2p (b), and O 1s (c) core level XPS spectra of the anatase TiO_2

the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ characteristic peaks of anatase TiO_2 could be observed at binding energy (BE) of 458.5 and 464.2 eV. O 1s XPS spectra of anatase TiO_2 are shown in Fig.7c, and the single O 1s peak can be resolved into two peaks at about 529.7 and 530.9 eV.

Fig.8 shows the Ti 2p and O 1s core level XPS spectra of Magnéli-phase titanium suboxides which were prepared at 950 °C, 25 min after hydrochloric acid leaching. As shown in Fig.8b, the two boarder peaks at about 458.5 and 464.6 eV correspond to binding energies of Ti $2p_{3/2}$ and Ti $2p_{1/2}$. The peak for Ti $2p_{3/2}$ could be deconvoluted into two peaks at about 458.5 and 459.2 eV. The peak at 458.5 eV is assigned to Ti^{4+} in TiO_2 lattice[31] and the peak at 459.2 eV is attributed to the Ti^{x+} ($x<4$). O 1s XPS spectrum of the as-prepared sample are shown in Fig.8c, and the single O1s peak is resolved into five peaks at 528.8, 529.5, 529.8, 531.2 and 532.2 eV. The two peaks between 528 and 530 eV are assigned to O L1 and O L2 in the anatase TiO_2 crystal lattice[31]. The peak at 531.2 eV corresponds to the oxygen bound to Ti^{x+}, further confirming more oxygen vacancies on the surface of as prepared sample. The peak at 532.2 eV was assigned to Ti-OH species[32]. According to the results of XPS analysis, it can be concluded that as-prepared Magnéli-phase titanium suboxides could increase the visible-light absorption of the photocatalysts because the surface of Magnéli-phase titanium suboxides forms oxygen vacancies.

2.3 SEM and TEM analysis of as-prepared Magnéli-phase titanium suboxides

Fig.9 shows the SEM morphology of the Magnéli-phase titanium suboxides, namely, the anatase-type TiO_2 reduced by Al for 25 min at 950 °C. The as-received Magnéli-phase titanium suboxides consists of nano-sized particles (about 400~600 nm). The particle size of as-prepared Magnéli-phase titanium suboxides almost does not grow compared with anatase titanium dioxide (particles typically 0.4~0.6 μm in diameter) because of lower sintering temperature and shorter sintering time.

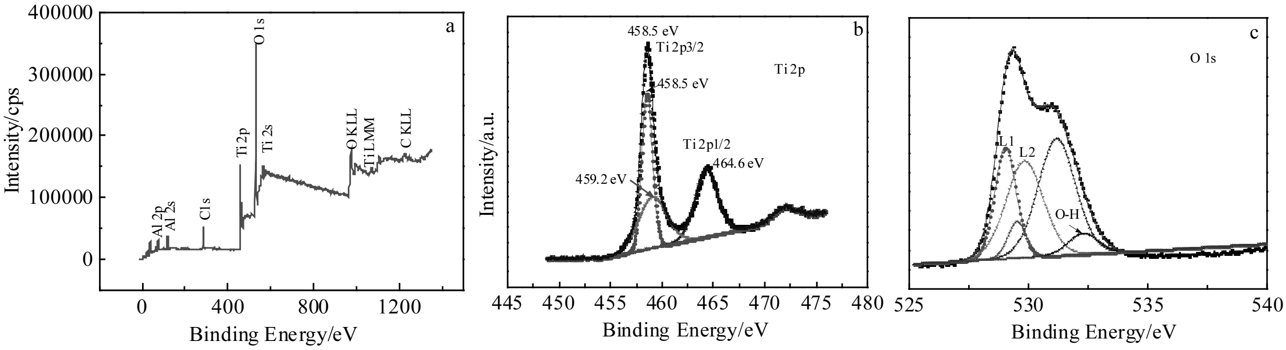

Fig.8 Full spectrum (a), Ti 2p (b), and O 1s (c) core level XPS spectra of the as-prepared Magnéli-phase titanium suboxides

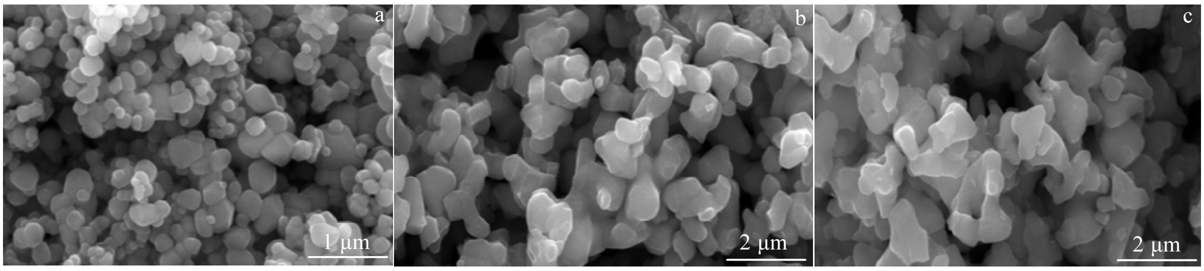

Fig.9 SEM images of the samples: (a)anatase TiO_2; (b)as-prepared Magnéli-phase titanium suboxides; (c)Magnéli-phase titanium suboxides after acid pickling

Fig.10 shows TEM image of the prepared Magnéli-phase titanium suboxides at 950 °C/10 min. The crystallite with an interplanar spacing of about 0.35 nm is fully consistent with the distance of (101) crystalline plane of the anatase TiO_2, and the interplanar appears to be surrounded by amorphous layers[33]. Fig.11 shows TEM and HRTEM images of prepared Magnéli-phase titanium suboxides (Ti_4O_7) at 950 °C/25 min and hydrochloric acid leaching. The SAED pattern well matched the reciprocal lattice of Ti_4O_7 in the zone axis of [101].

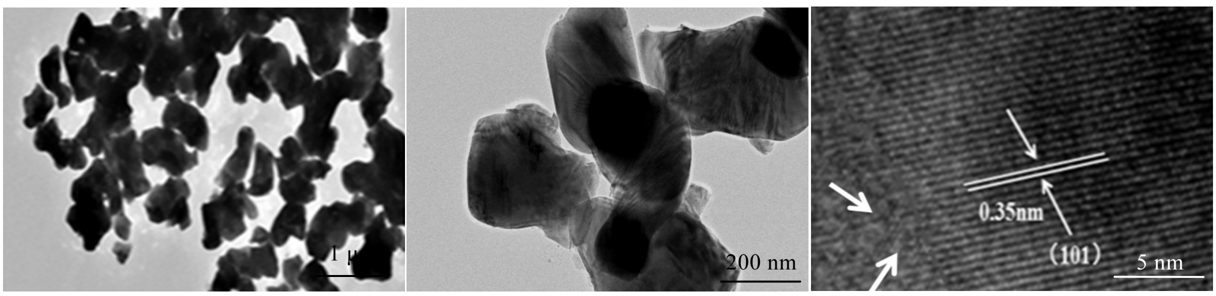

Fig.10 TEM and HRTEM images of the titanium suboxides as prepared at 950 °C/10 min

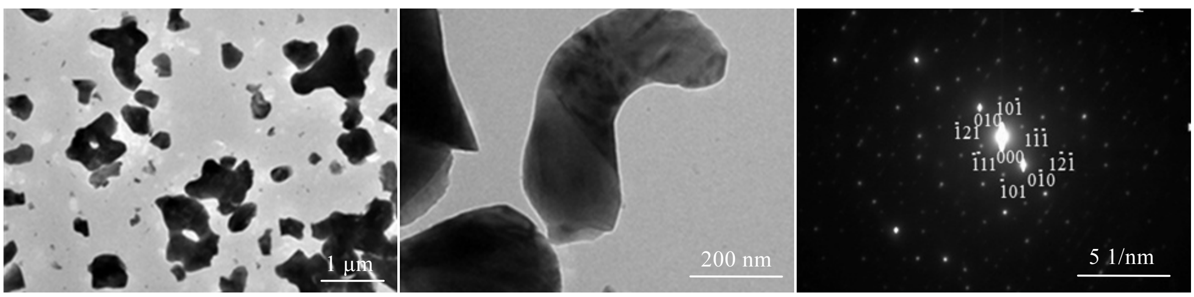

Fig.11 TEM images and SAED pattern of the titanium suboxides as prepared at 950 °C/25 min after hydrochloric acid leaching

2.4 Optical absorption spectra of as-prepared Magnéli-phase titanium suboxides

To research optical absorption of the as-prepared Magnéli-phase titanium suboxides, we measured the absorption spectra of the samples by UV-vis diffuse reflectance spectrum from 200 nm to 800 nm at room temperature. Fig.12a displays the UV-vis diffuse reflectance spectra for as-prepared Magnéli-phase titanium suboxides. It exhibits strong absorption increase with the increase of the roasting time. The forbidden band widths of anatase TiO_2 and rutile TiO_2 are 3.2 and 3.0 eV. Defect-free TiO_2 requires ultra violet light excitation due to its large band gap. Anatase TiO_2 in fact shows oxygen depletion upon aluminum reduction, resulting in band-gap narrowing of TiO_2, and thus high absorption of visible light. The three as-prepared Magnéli-phase titanium suboxides are black, further supporting the results of UV-vis diffuse reflectance.

The equations of forbidden band (E_g) of semiconductor be expressed as Eq.(3).

$$ahv = C\left(hv - E_g\right)^2 \tag{3}$$

We could draw the diagram according to measured data of DRS, such as Fig.12b. The value of the X-axis corresponding to the tangent is the forbidden band width of the sample which was reduced at 950 °C for 35 min. The value of forbidden band width is 1.9 eV.

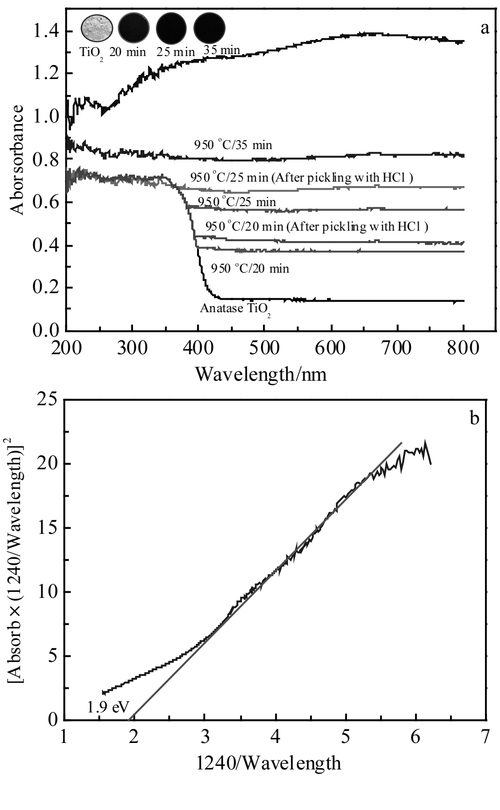

Fig.12 Absorption spectra of Magnéli-phase titanium suboxides samples reduced at different sintering time (a); forbidden band width of the sample which was reduced at 950 °C, for 35 min (b)

2.5 Visible light photocatalytic activity test

The as-prepared Magnéli-phase titanium suboxides samples are expected to exhibit considerable photocatalysis enhancement in comparison to pure anatase TiO_2 (A-TiO_2). Next, methylene blue (MB) was used as a probe to investigate the photocatalytic performance of the prepared samples, and A-TiO_2 was used as a reference sample. Concentration of methylene blue (MB) was 2 mol/L, volume of methylene blue was 150 mL and catalyst dosage was 5 mg. MB shows a maximum absorption at about 665 nm. The degradation efficiency of the samples was defined as C/C_0, where C and C_0 stand for the remnants and initial concentration of MB, respectively. Visible light photocatalytic decomposition experiments of MB were conducted using a 420 nm cut off filter, and the results are shown in Fig.13.

The degradation efficiency of 37%, 43%, and 62% was achieved for the as-prepared Magnéli-phase titanium suboxides samples after visible light irradiation for 130 min, and the degradation efficiency of A-TiO_2 was zero. The photocatalytic efficiency of sample which was reduced 950 °C for 35 min was found to be higher compared to samples of 20 and 25 min. This result suggests that the presence of the higher concentration of oxygen vacancy is preferable for the higher activity under visible light.

2.6 Proposed mechanism

Magnéli phase titanium suboxides with Ti_4O_7 as the mother phase could be prepared by the aluminum reduction-hydrochloric acid leaching route. Anatase TiO_2 in fact shows oxygen depletion upon aluminum reduction, resulting in band-gap narrowing of TiO_2, and thus high absorption of visible light. The possible photocatalytic processes are as follows:

$$Ti_4O_7 + hv = e^- + h^+ \tag{4}$$

$$e^- + O_2 = \bullet O_2^- \tag{5}$$

$$h^+ + H_2O = \bullet OH \tag{6}$$

$$\bullet OH, \bullet O_2^- + MB = CO_2 + H_2O + \text{Other prouducts} \tag{7}$$

Firstly, the electrons (e^-) in valence band of Ti_4O_7 under visible light irradiation could be excited to the conduction

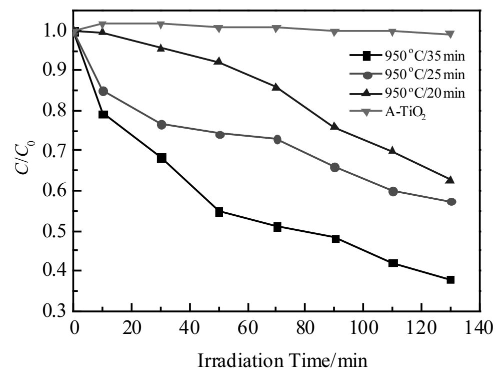

Fig.13 Concentration of methylene blue (MB) remained in the solution C/C_0 with irradiation time of visible light

band, leaving the holes (h^+) in valence band of Ti_4O_7 in Eq.(4). Then, the electrons might be also generated from the Ti_4O_7 particles with the product easily reacting with the adsorbed oxygen molecules to produce $\bullet O_2^-$ in Eq.(5). Meanwhile, the photogenerated holes as the strong oxidants could oxidize H_2O to $\bullet OH$ radicals (Eq.(6)). Finally, the MB is oxidized into carbon dioxide and water by these highly active $\bullet OH$ and $\bullet O_2^-$ radical species.

Based on the above results and analysis, a possible mechanism of the visible photocatalytic performance of Magnéli phase titanium oxide is schematically shown in Fig.14.

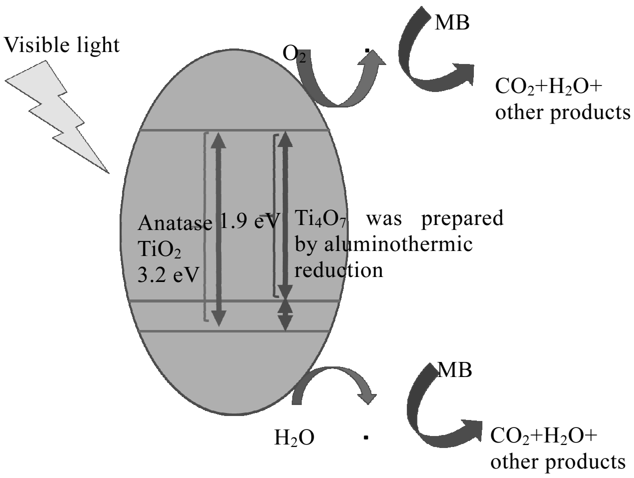

Fig.14 Mechanism of the MB oxidation over the Ti_4O_7 photocatalyst under visible light irradiation

3 Conclusions

1) Magnéli phase titanium suboxides whose mother phase was Ti_4O_7 were successfully prepared by an aluminum reduction-hydrochloric acid leaching route. The as-prepared Magnéli phase titanium oxide shows strong absorption in visible-light region.

2) A large amount of oxygen vacancies appear on the surface of Magnéli phase titanium oxide, which accounts for the enhanced visible-light absorption performance. The synthesized Ti_4O_7 material retains the diameters of the pristine TiO_2, which is 400~600 nm. The degradation efficiency of 37%, 43%, and 62% is achieved for the as-prepared Magnéli-phase titanium suboxides samples after visible light irradiation for 130min, and the degradation efficiency of A-TiO_2 is zero.

3) The photocatalytic efficiency of sample which is reduced at 950 °C for 35 min is found to be higher compared to samples for 20 and 25 min.

References

1 Kitada A, Hasegawa G, Kobayashi Y *et al*. *Journal of the American Chemical Society*[J], 2012,134(26): 10894
2 Grätzel M. *Nature*[J], 2001, 414(6861): 338
3 Hoffmann M R, Martin S T, Choi W Y *et al*. *Chemical Reviews*[J], 1995, 95(1): 69
4 Lu G, Linsebigler A, Yates J T. *Journal of Physical Chemistry*[J], 1995, 99(19): 7626
5 Chen X, Mao S S. *Cheminform*[J], 2007, 38(41): 2891
6 Zou Z, Ye J, Sayama K *et al. Nature*[J], 2001, 414(6864): 625
7 Anpo M, Ichihashi Y, Takeuchi M *et al*. *Research on Chemical Intermediates*[J], 1998, 24(2):143
8 Irie H,Watanabe Y, Hashimoto K. *Journal of Physical Chemistry B*[J], 2003, 107(23): 5483
9 Choi Y, Umebayashi T, Yoshikawa M. *Journal of Materials Science*[J], 2004, 39(5): 1837
10 Shen M, Wu Z, Huang H *et al*. *Materials Letters*[J], 2006, 60(5): 693
11 Asahi R, Morikawa T, Ohwaki T *et al*. *Science*[J]. 2001, 293(5528): 269
12 Torbjörn L, Mwabora J M, Avendaño J *et al*. *The Journal of Physic Chemistry B*[J], 2007, 107(24): 5709
13 Umebayashi T, Yamaki T, Itoh H *et al*. *Applied Physics Letters*[J], 2002, 81(3): 454
14 Jia L, Wu C, Li Y *et al*. *Applied Physics Letters*[J], 2011, 98(21): 2815
15 Qi Kezhen, Cheng Bei, Yu Jiaguo *et al*. *Chinese Journal of Catalysis*[J], 2017, 38(12): 1936
16 Lu L Y, Wang G H, Zou M *et al. Applied Surface Science*[J], 2018 , 441: 1012
17 Wang J, Wang G H, Wang X *et al. Carbon*[J], 2019, 149:618-626.
18 Wang J, Wang G H, Wei X H *et al. Applied Surface Science*[J], 2018, 456: 666
19 Liu G, Wang G H, Hu Z H *et al. Applied Surface Science*[J], 2019, 465: 902
20 Andersson S, Collén B, Kuylenstierna U *et al*. *Acta Chemica Scandinavica*[J], 1957, 11(10):1641
21 Murray J L, Wriedt H A. *Journal of Phase Equilibria*[J]. 1987, 8(2):148
22 Toyoda M, Yano T, Tryba B *et al*. *Applied Catalysis B: Environmental*[J], 2009, 88(1): 160
23 Tsumura T, Kojitani N, Izumi I *et al. Journal of Materials Chemistry*[J], 2002,12(5): 1391
24 Inagaki M, Nonaka M, Kojin F *et al. Environmental Technology*[J], 2006, 27(5): 521
25 Smith J R, Walsh F C, Clarke R L. *Journal of Applied Electrochemistry*[J],1998, 28(10): 1021
26 Tang C, Zhou D B, Zhang Q. *Materials Letters*[J], 2012, 79: 42
27 Zhu R J, Liu Y, Ye J W *et al*. *Journal of Materials Science Materials in Electronics*[J], 2013, 24(12): 4853
28 Hauf C, Kniep R, Pfaff G. *Journal of Materials Science*[J], 1999, 34(6): 1287

29 Kolbrecka K, Przyluski J. *Electrochimica Acta*[J], 1994, 39(11): 1591

30 Acha C, Monteverde M, Nunez R M *et al. The European Physical Journal B-Condensed Matter and Complex Systems*[J], 2003, 34(4): 421

31 Zhuang J, Weng S, Dai W *et al. Journal of Materials Chemistry C*[J], 2012,116(116): 25354

32 Zhang Z, Zhou Z, Nie S *et al. Journal of Power Sources*[J], 2014, 267(4): 388

33 Chen X B, Liu L, Yu P Y *et al*. *Science*[J], 2011, 331(6018): 746

铝热还原法制备 Magnéli 相亚氧化钛及其可见光光催化活性研究

李 军，吴恩辉，侯 静，黄 平，蒋 燕，徐 众，刘黔蜀

（攀枝花学院 攀枝花国际钒钛研究院, 四川 攀枝花 617000）

摘　要：采用铝热还原-盐酸酸洗工艺成功制备了 Magnéli 相亚氧化钛，通过 XRD, SEM, UV-Vis DRS 和 XPS 等手段进行表征。结果表明：在焙烧温度 950 ℃，焙烧时间 20 min，Al/TiO_2=0.2 时，成功制备以 Ti_4O_7 为主要物相的 Magnéli 相亚氧化钛材料，其粒径为 400~600 nm，样品表面形成了大量的氧空位，表现出很强的紫外和可见光吸收性能。在可见光条件下光照 130 min 时，950 ℃焙烧 20、25 和 35 min 条件下制备并酸洗后的 Magnéli 相亚氧化钛降解亚甲基蓝的效率分别达到 37%、43%和 62%。

关键词：铝热还原；Magnéli 相；光催化降解

作者简介：李 军，男，1986 年生，博士，助理研究员，攀枝花学院，四川 攀枝花 617000, E-mail: lidejun163@126.com