

University of Groningen

Micro-patterned TiO₂ films for photocatalysis

Liu, Jiaqi; Liu, Hongwu; Zuo, Xiaodan; Wen, Feng; Jiang, Hong; Cao, Huatang; Pei, Yutao

Published in:
Materials Letters

DOI:
[10.1016/j.matlet.2019.07.098](https://doi.org/10.1016/j.matlet.2019.07.098)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2019

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Liu, J., Liu, H., Zuo, X., Wen, F., Jiang, H., Cao, H., & Pei, Y. (2019). Micro-patterned TiO₂ films for photocatalysis. *Materials Letters*, 254, 448-451. <https://doi.org/10.1016/j.matlet.2019.07.098>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.



Micro-patterned TiO₂ films for photocatalysis

Jiaqi Liu^a, Hongwu Liu^a, Xiaodan Zuo^a, Feng Wen^{a,b,*}, Hong Jiang^{a,b}, Huatang Cao^c, Yutao Pei^c

^aSchool of Materials Science and Engineering, Hainan University, Haikou 570228, P.R. China

^bSpecial Glass Key Lab of Hainan Province, Haikou 570228, P.R. China

^cDepartment of Advanced Production Engineering, Engineering and Technology Institute Groningen, University of Groningen, Nijenborgh 4, 9747 AG, the Netherlands

ARTICLE INFO

Article history:

Received 12 June 2019

Received in revised form 9 July 2019

Accepted 24 July 2019

Available online 25 July 2019

Keywords:

Titanium dioxide film

Structural

Photocatalysis

Mass transfer

Photolithography

Physical vapour deposition

ABSTRACT

Titanium dioxide film as a stable material plays an important role in photocatalytic degradation of pollutants. One of the ways to improve photocatalytic efficiency is to increase the active sites on the semiconductor surface. Photolithography is a manufacturing technique for controlling precisely micrographics on surface. Here grating-structured, square-structured and hexagon-structured TiO₂ films were prepared by photolithography and the effects of various surface structures on photocatalysis were studied. It was demonstrated that the photocatalytic activity of TiO₂ film was not always improved as the surface area increased. The micro-patterned surface would also impede the mass transfer in the process of photocatalysis.

© 2019 Elsevier B.V. All rights reserved.

1. Introduction

Up to now, the application of titanium dioxide (TiO₂) in photodegradation of organic contaminants, batteries and solar cells has attracted significant attention due to its unique characteristics and environmental friendliness [1]. However, most TiO₂ photocatalysts developed are present in powder form and thus have limitations for practical or industrial applications. The development of stable and easily applicable thin film photocatalysts is therefore strongly desired [2].

In terms of prevalent TiO₂ films, they exhibit high stability in aqueous solutions, no photo corrosion under bandgap illumination, as well as exceptional surface properties [3]. But the less specific surface area restricted the photocatalytic efficiency of films. It is well known that the augment of the photocatalysis active sites is an alternative path to enhance photocatalytic efficiency [4]. Recently, self-organized nanocrack networks were fabricated to enlarge catalytic surface area in sputtered TiO₂ thin films [5]. Importantly, the amount of surface active sites is not the only factor in the process of photocatalysis [6]. If the increase in surface area would affect some other steps in the process is not very clear.

Among the required processes for micro-nanometer fabrication, lithography is one of core issues. Photolithography with recent remarkable improvement has contributed to the industry during the past few decades [7]. One of the merits of photolithography is the precise structural control. Herein, we fabricated several different structured substrates with the method of photolithography and prepared TiO₂ films on them. The effects of surface structures on photocatalytic performance were investigated in detail.

2. Materials and methods

Silicon (1 1 0) wafers were ultrasonically cleaned by a sequence of liquids, including acetone, ethyl alcohol and deionized water, each for 10 min respectively. At first, the positive photoresist (SUN-125PSS, SUNTIFIC) was sprayed (see Fig. S1 for the parameters) rotationally on the silicon substrate before baking of 100 s at 100 °C. To fabricate surface patterns, a 390 nm light was used to irradiate the photoresist in an optical direct-write lithography system (uPG501, Heidelberg, Germany), with the optimal parameters of 56 ms exposure and 5 for Defoc value. After that, the wafer was put into the developing solution (SUN-238D, SUNTIFIC) for 30 s, rinsed with deionized water and followed by 120 s baking at 120 °C. The process of pattern transfer was proceeded by using ion beam etching (Table S1). At the end, Ti-O amorphous film was deposited on the patterned Si substrate by magnetron

* Corresponding author at: School of Materials Science and Engineering, Hainan University, Haikou 570228, P.R. China.

E-mail address: fwen323@hainanu.edu.cn (F. Wen).

sputtering (Table S2) and the wafer with Ti-O film was annealed for 2 h at 400 °C. The main process was illustrated in Scheme S1.

3. Results and discussion

Fig. 1 shows the microstructure of TiO₂ films deposited on the patterned surface of silicon wafers. All the actual shapes were almost in accord with the designed patterns. Unlike the planar film, all the films deposited on patterned Si substrates were rough. It was because that the particle bombardment led to surface defects. Fortunately, the rough surface would further contribute to large surface area on the basis of the area contribution of patterned structures. According to the cross-sectional view, the thickness of TiO₂ films on plane was about 1.48 μm, which was slightly thicker than that of films on the trench and side wall. And in terms of the nonperpendicularity on profiles (see the amplification in Fig. 1b–d), the reason why it existed was the reduce in margin of the photoresist over etching time. The height of every concave-convex structure remained at about 5 μm (see also Fig. S3), which depended on the thickness of photoresist.

The GIXRD pattern shown in Fig. 1e confirmed a mixture of anatase and rutile phases formed in the TiO₂ film. High resolution XPS analysis (Fig. 1f) in the zone of Ti 2p signals revealed that TiO₂ films had the double signal of the system Ti 2p_{3/2} and Ti 2p_{1/2} at 458.4 and 464.1 eV, respectively [8]. Both results illustrated that as-prepared films presented the characteristics of TiO₂.

It is well known that the surface area is the key to photocatalytic capacity [9]. The concave and convex structures were beneficial to increase the total surface area. The ratio (denote as R) of actual surface area over nominal area was shown in Fig. 2. There was a ~15% increase in surface area for the grating-structured TiO₂ film, and ~22% and ~25% increase for the square-structured and the hexagon-structured TiO₂ film, respectively.

The results of water contact angle tests illustrated the interaction between the surface and water droplet. As can be seen in Fig. 2, the planar TiO₂ film exhibited a slight hydrophobicity, with a contact angle of about 92°. The water contact angle dropped to 15–25° by micro-patterning that changed the wetting behavior of TiO₂ films to more hydrophilicity. It was the patterned structures that worked: the water droplet tended to spread out by the trench.

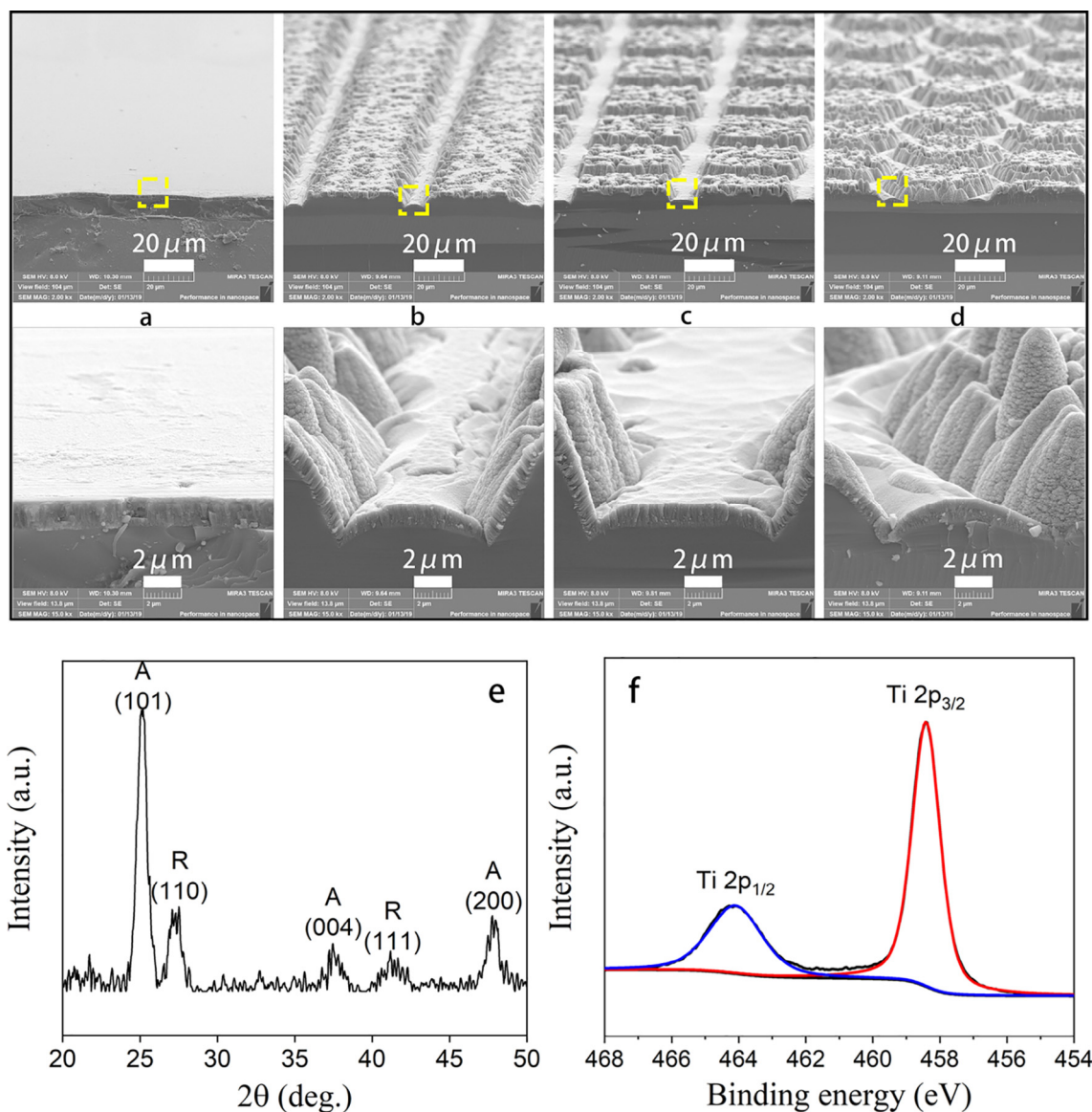


Fig. 1. SEM images of (a) planar TiO₂ film, (b) grating-structured TiO₂ film, (c) square-structured TiO₂ film, and (d) hexagon-structured TiO₂ film. The amplification of corresponding regions (dotted box) is also shown here. (e) GIXRD pattern of the TiO₂ film (A: Anatase and R: Rutile), (f) Ti 2p region XPS spectrum of the TiO₂ film.

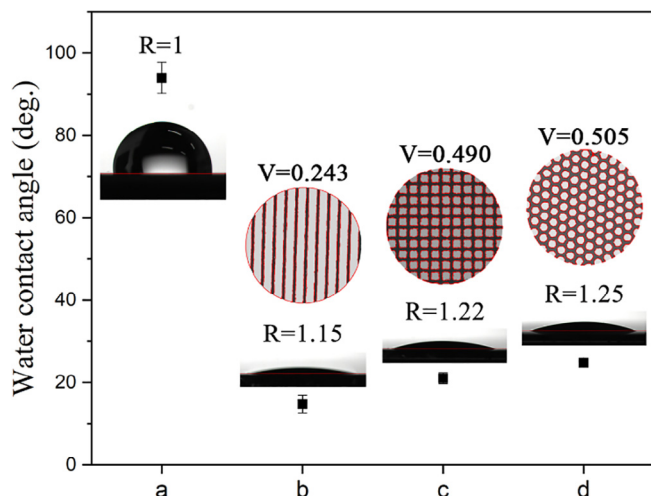


Fig. 2. Water contact angle along with the ratios (R) of actual surface area over nominal area of (a) planar TiO₂ film, (b) grating-structured TiO₂ film, (c) square-structured TiO₂ film and (d) hexagon-structured TiO₂ film in an area of $0.5 \times 0.5 \text{ mm}^2$. The ratios (V) of the projected area of trench over the whole round area of three patterned structures are also shown.

In this case, the volume in the trenches needed to be considered in order to describe the wettability in detail. Then, it was only crucial to calculate the projected area of trenches on account of the same height of trench. Consider that the droplet projection is round, the area ratio of trench was analyzed in a specific circle (Fig. 2). The volume in the trenches was proportional to the projected area of trenches. So, the hexagon-structured TiO₂ film possessed the largest volume of trench in a particular nominal area, compared with other patterned structures. This trait enabled it to accommodate more droplet than others so that the area of diffusion reduced, showing large contact angle. From a view of energy, gravitational potential energy provides the diffusion force of droplet, and the spread terminates when the diffusion resistance exceeds the diffusion driving force.

Photocatalytic activity of various TiO₂ films were assessed by monitoring the degradation of methyl orange (MO, a model organic dye) in water under ultraviolet light irradiation (254 nm) (Fig. 3). Compared with the planar TiO₂ film, all the structured TiO₂ films possessed better photocatalytic capability, attributed to the increase in reactive sites on the surfaces. It can be seen that the

catalytic efficiency of square-structured TiO₂ film was higher than that of other structural films. Furthermore, the grating-structured TiO₂ film had a smaller surface area but seemed to have same photocatalytic properties as the hexagon-structured TiO₂ film. It was demonstrated that not only the total surface area acted as the key to photocatalysis, the structure of trench on the surface also played a significant role in photocatalysis. Because the liquid in the trenches was subject to more resistance from the side wall than the liquid on the plane, the flow velocity of liquid in the trenches was slower than elsewhere. Mass transfer of the organic pollutants through diffusion between the bulk solution and the surface of the semiconductor is a vital step in the reaction pathways for the eventual decomposition of the pollutants [10]. The mass exchange rate in the trench structure was hindered by the poor mobility of fluid. Analogously, in the photocatalytic degradation of toluene, a diverse ratio in the quantity of reactants resulted in the generation of the different chemical species [11,12]. Therefore, a structure with a large proportion of trenches would restrain the efficiency of dye degradation.

4. Conclusions

The present work analyzed the effects of structured TiO₂ films on photocatalytic capacity. It was found that the rate of decomposition of the pollutants didn't always increase with the increasing surface area, because the trenches impeded the mass transfer step in the process of photocatalysis. Therefore, the square-structured TiO₂ films exhibited highest photocatalytic activity compared to other films. The effects of hydrodynamics on photocatalysis need to be further studied.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the Key Research and Development Project (ZDYF2019206, China), National Natural Science Foundation of China (51461015, China) and the Postgraduate Innovation Foundation of Hainan Province (Hys2018-51, China).

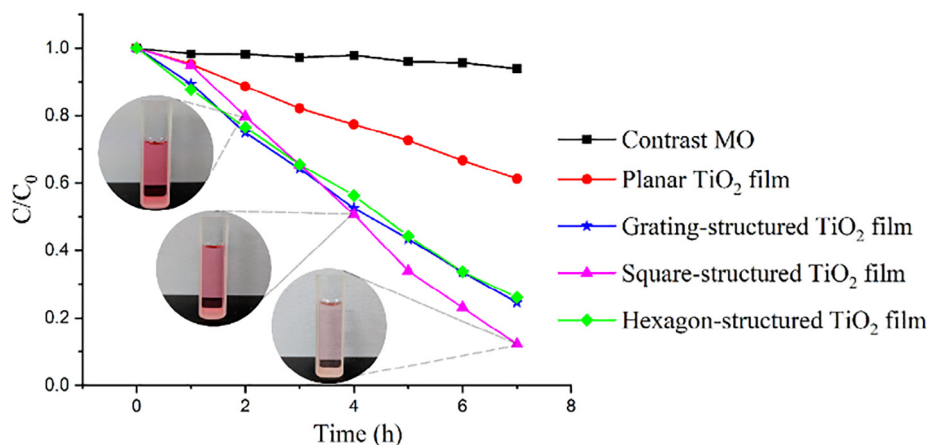


Fig. 3. Photocatalytic degradation of MO under ultraviolet light (254 nm) irradiation. C and C_0 represent the real-time and initial concentration of methyl orange solution. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2019.07.098>.

References

- [1] Z. Shayegan, C.-S. Lee, F. Haghghat, TiO₂ photocatalyst for removal of volatile organic compounds in gas phase – a review, *Chem. Eng. J.* 334 (2018) 2408–2439, <https://doi.org/10.1016/j.cej.2017.09.153>.
- [2] J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, D.W. Bahnemann, Understanding TiO₂ photocatalysis: mechanisms and materials, *Chem. Rev.* 114 (2014) 9919–9986, <https://doi.org/10.1021/cr5001892>.
- [3] G. Varshney, S.R. Kanel, D.M. Kempisty, V. Varshney, A. Agrawal, E. Sahle-Demessie, R.S. Varma, M.N. Nadagouda, Nanoscale TiO₂ films and their application in remediation of organic pollutants, *Coord. Chem. Rev.* 306 (2016) 43–64, <https://doi.org/10.1016/j.ccr.2015.06.011>.
- [4] M. Ge, J. Cai, J. Iocozzia, C. Cao, J. Huang, X. Zhang, J. Shen, S. Wang, S. Zhang, K.-Q. Zhang, Y. Lai, Z. Lin, A review of TiO₂ nanostructured catalysts for sustainable H₂ generation, *Int. J. Hydrogen Energy.* 42 (2017) 8418–8449, <https://doi.org/10.1016/j.ijhydene.2016.12.052>.
- [5] B. Henkel, A. Vahl, O.C. Aktas, T. Strunskus, F. Faupel, Self-organized nanocrack networks: a pathway to enlarge catalytic surface area in sputtered ceramic thin films, showcased for photocatalytic TiO₂, *Nanotechnology* 29 (2017) 35703, <https://doi.org/10.1088/1361-6528/aa9d35>.
- [6] W.-J. Ong, L.-L. Tan, Y.H. Ng, S.-T. Yong, S.-P. Chai, Graphitic carbon nitride (g-C₃N₄)-based photocatalysts for artificial photosynthesis and environmental remediation: are we a step closer to achieving sustainability?, *Chem Rev.* 116 (2016) 7159–7329, <https://doi.org/10.1021/acs.chemrev.6b00075>.
- [7] J.U. Kim, S. Lee, T.-I. Kim, Recent advances in unconventional lithography for challenging 3D hierarchical structures and their applications, *J. Nanomater.* 2016 (2016) 7602395.
- [8] J. Matharu, G. Cabailh, G. Thornton, Synthesis of TiO₂(110) ultra-thin films on W(100) and their reactions with H₂O, *Surf. Sci.* 616 (2013) 198–205, <https://doi.org/10.1016/j.susc.2013.05.020>.
- [9] S.G. Ullattil, S.B. Narendranath, S.C. Pillai, P. Periyat, Black TiO₂ nanomaterials: a review of recent advances, *Chem. Eng. J.* 343 (2018) 708–736, <https://doi.org/10.1016/j.cej.2018.01.069>.
- [10] G. Mamba, A.K. Mishra, Graphitic carbon nitride (g-C₃N₄) nanocomposites: a new and exciting generation of visible light driven photocatalysts for environmental pollution remediation, *Appl. Catal. B Environ.* 198 (2016) 347–377, <https://doi.org/10.1016/j.apcatb.2016.05.052>.
- [11] M.J. Muñoz-Batista, A. Kubacka, M.N. Gómez-Cerezo, D. Tudela, M. Fernández-García, Sunlight-driven toluene photo-elimination using CeO₂-TiO₂ composite systems: a kinetic study, *Appl. Catal. B: Environ.* 140–141 (2013) 626–635, <https://doi.org/10.1016/j.apcatb.2013.04.071>.
- [12] M.J. Muñoz-Batista, A. Kubacka, A.B. Hungria, M. Fernández-García, Heterogeneous photocatalysis: light-matter interaction and chemical effects in quantum efficiency calculations, *J. Catal.* 330 (2015) 154–166, <https://doi.org/10.1016/j.jcat.2015.06.021>.