

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

COMMUNICATION

A novel preparation of Ag-doped TiO₂ nanofibers with enhanced stability of photocatalytic activity

Cite this: DOI: 10.1039/x0xx00000x

Fanli Zhang^{a,1}, Zhiqiang Cheng*^{a,b,1}, Lijuan Kang^a, Liying Cui^a, Wei Liu^a

Received 00th January 2012,

Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

, Xiaojuan Xu^a, Guohui Hou^a, Hongjia Yang^a

Hierarchical structure with high densities of secondary Ag nanoparticles grown on primary TiO₂ fibers have been got by the facile and low-cost way of combination of electrospinning and hydrothermal technique. The property of photocatalysis was verified by degradation of Rhodamine B (RhB), and exhibited high efficiency and stability under UV-light illumination.

Titanium dioxide has attracted lots of attention in past decades for the discovery of photocatalytic splitting of water under ultraviolet light by Honda and Fujishima in 1972¹. To date, TiO₂ has been proven to be the promising semiconductor catalyst and one of the excellent photocatalysts for degradation of organic contaminant in environment²⁻⁴ due to the significantly low energy consumption, friendly operation conditions, high oxidizing power, low cost and nontoxicity in the process of applications^{5, 6}. Therefore, it has been applied in many areas, such as solar cell⁷, gas sensor⁸, and other fields. However, there are also some defects for the application of TiO₂. The main drawbacks of TiO₂ photocatalyst are the lack of visible light and high rate recombination of hole-electron for the large band gap of TiO₂⁹⁻¹⁰ (3.2 eV in anatase phase). Numerous scientific researchers have made great progress for the enhancement of photocatalytic efficiency to overcome these drawbacks, whereas it is complex, high energy-cost, and hard to industrial production¹¹. However, all of researches to enhance the activity of TiO₂ could be divided into three aspects. First, some researches were about to improve the quantum yield and it is noting that the crystal structure¹², hydroxyl groups on the surface, exposed facets and oxygen deficiencies have significant influence on it¹³⁻¹⁸. Second, attempts to extend light absorption from UV region into visible spectrum have made some progresses and enhanced the photocatalytic activity greatly. Third, some of workers intend to suppress the recombination of electron-hole pairs in TiO₂, such as depositing noble metals and coupled semiconductor heterostructure¹⁹⁻²¹. In our work, a facile method was put forward to produce the heterostructure of silver and

TiO₂ at a cost-effective way combining electrospinning with hydrothermal process. Electrospinning technique has gained increasing appeal as a versatile technique for fabricating the nano- and sub-micron fibers possessing the feature of large surface-to-volume ratio²². The first preparation of TiO₂ fibers through electrospinning was reported by Li D et al²³. Since then, there were lots of studies about fabrication of TiO₂ fibers in employing sol-gel electrospinning, including dopant of silver for enhancing the properties of TiO₂ in applications²⁴⁻²⁶ and appearing higher reactivity than pure TiO₂. Driven by these studies, lots of innovative approaches have been developed to synthesize the TiO₂-based heterostructures²⁷⁻²⁹. Unfortunately, there is hardly any research which could ensure the large demand for industrial production. It is worth noting that exploration of nano-sized Ag to modify TiO₂ is of great interest in photocatalytic applications, because Ag could serve as electron scavenging center to separate electron (e⁻)-hole (h⁺) pair for its lower Fermi level than conduction band of TiO₂. Additionally, small silver particles have the ability to generate surface plasmon resonance with TiO₂³⁰, thus leading to a markedly enhanced photocatalytic activity of TiO₂ fibers and an increased quantum yield for photocatalytic processes.

In this communication, we firstly report an effective three-step route by the combination of electrospinning and hydrothermal method to synthesize Ag/TiO₂ hierarchical structures which is probably contributing to enhancing the electron-hole separation and interfacial charge transfer. Firstly, we got the anatase TiO₂ fibers (after calcination) by electrostatic spinning. Secondly, the TiO₂ fibers were put into AgNO₃ solution under UV illumination for 5 mins. Thirdly, the TiO₂ fibers treated by AgNO₃ solution were mixed with specific concentrations of Ag⁺ and HMTA aqueous solution in reaction kettle under 90 °C for 10 h. The first step is to produce the TiO₂ fibers which have large specific surface area and provide the platform for the deposition of Ag crystal nucleus in the second step. The second step is to get the Ag crystal nucleus for providing the growth direction of silver.

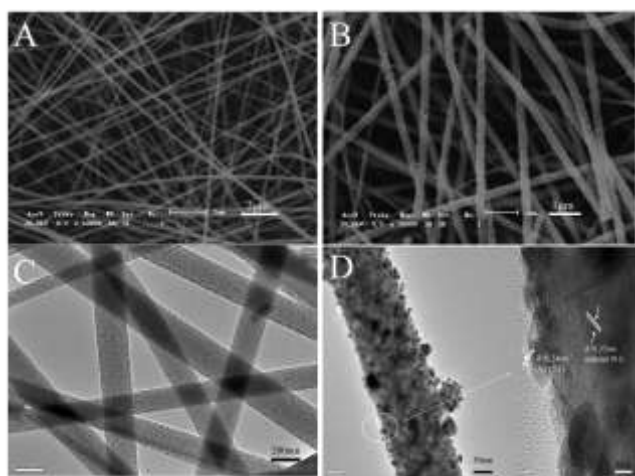


Figure 1: A pure TiO₂ fibers; B Ag/TiO₂ films were in hydrothermal process with concentrations of 0.01M; C TEM image of TiO₂ fibers; D TEM(left) and HRTEM(right) image of Ag/TiO₂ fibers(0.01M AgNO₃ solution).

Fig. 1A presents an SEM image of the pure TiO₂ fibers, which were fabricated by electrospinning equipment followed by calcination at 520 °C (Fig.S1, ESI†) for 4 hours²⁰. The fibers were in sub-micron or nanoscale in diameter and it can be clearly seen that the TiO₂ fibers (Fig. 1A and Fig. 1C) are of relative smooth surface without secondary structures. Simultaneously, the porous between fibers made it possible for the uniform growth of silver³¹. Then, the pure TiO₂ fiber was immersed in AgNO₃ solution for 4h at home temperature to get stable equilibrium for absorbing and desorbing Ag⁺; after that, the fibers treated by Ag⁺ were irradiated with ultraviolet light for 5 minutes. (Figure S2A, ESI†) At last, the hydrothermal reaction was carried out at 90 °C to obtain the hierarchical Ag/TiO₂ nanostructures (Fig. 1B) with different concentration of Ag⁺ in reaction solution. It is worth noting that the AgNPs adhered on the surface tightly which would not come off during the ultrasonic process. As we can see from the SEM images of as-prepared products (Fig.S2B and S2C ESI†), with the concentration of Ag⁺ increasing, the higher density of secondary Ag nanoparticles would adhere on the TiO₂ substrates uniformly. It is interesting that we will not get the hierarchical nanostructures without the second step; the Ag crystal nucleus provided the orientations for the growth of Ag³². As we all know, the properties of Ag/TiO₂ structures depend highly on the densities of Ag, such as the electrical property, photocatalytic property etc. In principle, the large size of particles' surface energies is lower than that of small size particles of Ag. So, the small Ag nanoparticles would incline to grow larger with the concentrations of reactants and reaction time continued via Ostwald ripening procedure³³. Therefore, by tuning the reactant concentrations, the morphology of products can be further controlled and the Ag/TiO₂ heterojunctions with different particle size of Ag will afford more opportunities for their potential applications. Fig. 1D shows the representative TEM (left inset) and high-resolution transmission electron microscopy (HRTEM, right inset) micrographs of Ag/TiO₂ heterostructures. As shown in the TEM image, large quantity of Ag nanocrystals are adhering on the surface of TiO₂ fibers and it can be seen that the size distribution of Ag was mainly contrasted at 5-35nm by calculating through the TEM image. Furthermore, the HRTEM image of Ag/TiO₂ fiber shows clear lattice fringe of $d=0.35\text{nm}$ (matching anatase (101) crystallographic plane) and $d=0.24\text{nm}$ (cubic phase of Ag (111) plane) in the right of Fig. 1D. Simultaneously, the border of Ag and

TiO₂ is invisible, which demonstrate that composition fusion may occur between the interface of TiO₂ and Ag as shown in HRTEM image of Fig. 1D.

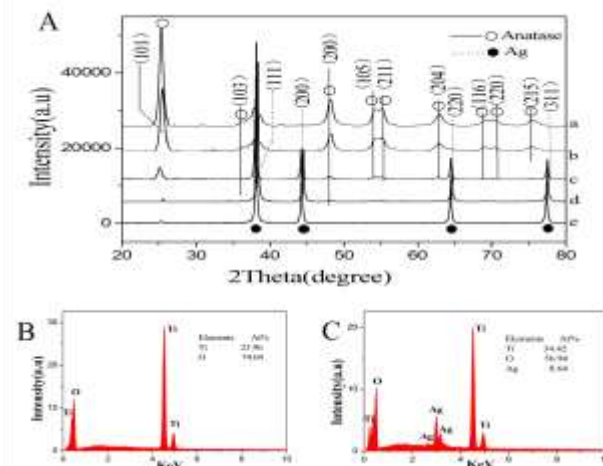


Figure 2: A the XRD patterns of samples (a: Pure TiO₂ fiber; b: Treated by UV illumination in AgNO₃ solution; c, d and e were in hydrothermal process with concentrations of 0.01M, 0.03M and 0.05M AgNO₃ respectively; B the EDS microanalysis on selected areas of the TiO₂ nanofibers; C The EDS microanalysis of selected Ag/TiO₂(0.01M AgNO₃ solution) heterostructures.

The energy dispersive X-ray (EDX) spectrometry clearly show the presence of Ti, O, and Ti, O, Ag elements on the surface of pure TiO₂ films(Fig. 2B) and Ag/TiO₂ films(Fig. 2C) respectively. Fig. 2A was the XRD patterns of the samples. As the results show that, all of the diffraction peaks can be readily indexed to anatase phase TiO₂ (Fig 2a and Fig 2b), and those main diffraction peaks have been indexed to JPCDS#21-1272²⁰. The corresponding crystal face indexes have marked in XRD patterns. Interestingly, the TiO₂ diffraction peaks would be disappeared with the increasing load of Ag particles on the TiO₂ surface. The curve e (Fig. 2A) indicated barely noticeable anatase diffraction peaks.

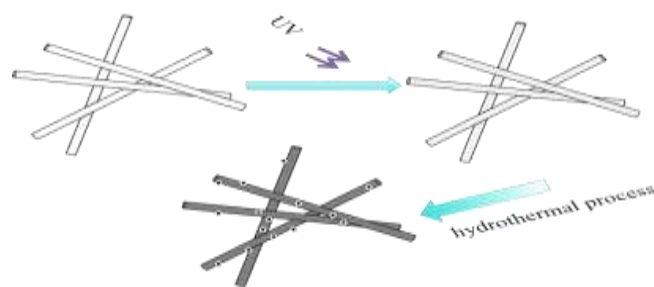
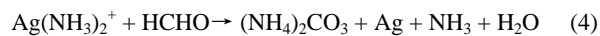
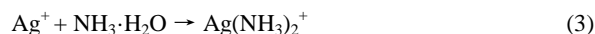
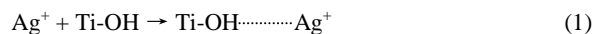


Figure 3: the schematic of synthesis process for Ag/TiO₂

The mechanism of synthesis for Ag/TiO₂ is simple. The fibers immersed in Ag⁺ solution would absorb the Ag⁺ on the TiO₂ surface according to the formula 1²⁴. Then the UV irradiation (254 nm) procedure sustained 5 mins and then the films were washed with ultrapure water and dried under vacuum drying oven. We can see the nanoparticles adhering on the fiber. As we knew that TiO₂ would produce the electrons and holes with the UV light and the electrons would reduce the silver ions into Ag on the surface of TiO₂ fiber. The nanoparticles of silver by photocatalytic reduction method could

provide the direction for Ag growth³⁴. After that, the TiO₂ fibers treated by second step were put in autoclave containing AgNO₃ and C₆H₁₂N₄. With the temperature increasing, the hexamine decomposes into ammonia and formaldehyde gradually³⁵ as the following formula 2. Then, ammonia combines with Ag⁺ and transforms into Ag(NH₃)₂⁺ ions (formula 3).



Moreover, the formaldehyde (CH₂O) which was from hexamine would reduce the silver ammonia complex ions into pure Ag growing along the same direction of the lattice of the silver crystal nucleus.

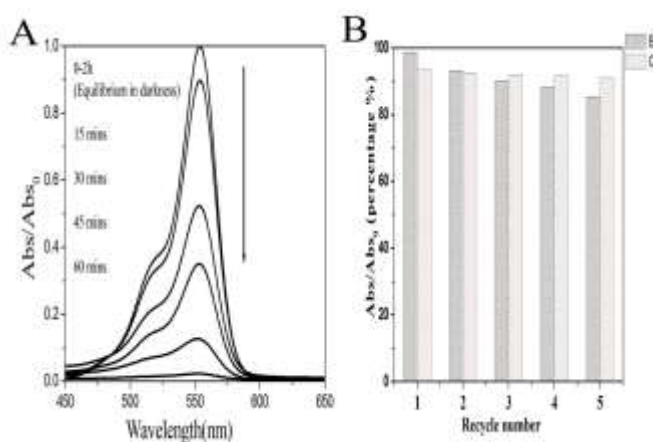


Figure 4: Curves of the photocatalytic degradation of RhB under UV light: A In the presence of the pure TiO₂ fibers; B The diagram of degradation ratio of RhB versus reuse times (B indicates the pure TiO₂ fibers, C represents Ag/TiO₂).

To testify the property of photocatalysis, we chose the RhB as degradation material under UV-vis light illumination (the main wavelength of lamp is about 365nm, 125W, Philips). As we can see from the Fig. 4A, there is no obvious shift of λ max in the photocatalysis process. Then, the mechanism of degradation process for RhB was discussed briefly in the supporting information³⁶ (Figure S4, ESI[†]). Meanwhile, we also investigated stabilities of the Ag/TiO₂ (0.01M AgNO₃) and pure TiO₂ fibers. The results showed that Ag/TiO₂ membrane exhibited more stable than pure TiO₂ fibers after five times reuse. Simultaneously, we have compared two kinds of morphology after reuse and the Ag/TiO₂ still remained good. As we know, Ag is noble metal which is more stable in the process of reaction than other materials, so during the photocatalytic degradation, it played an important role in corrosion resistance³². As we can see from the Figure 4B, the photocatalytic efficiency of Ag/TiO₂ heterostructure (Figure S3, ESI[†]) is slightly lower than that of pure TiO₂ films. It is because that some particles of Ag on the surface of TiO₂ may block ultraviolet absorption and reduce the photogenerated electron-hole pairs, then lower the TiO₂ fibers photoactivity.³⁷ In other case, the size of Ag particles also plays a

great role in the photocatalytic activity. The Ag would occupy the active sites of TiO₂ fibers surface and cause the TiO₂ lower its activity. Simultaneously, the photogenerated electrons on the silver sites would attract holes and recombine together³⁸. In this case, the Ag particles adhering on the surface of TiO₂ fibers would be the e⁻-h⁺ pair recombination centers³⁹. At the same time, the probability of the hole-capture would be increased by the excessive coverage of silver particles, which decrease the probability of holes reacting with adsorbed RhB at the TiO₂ fiber surface.⁴⁰ However, the deposition of Ag nanoparticles on TiO₂ photocatalyst can also highly improve its photocatalytic efficiency through the schottky barrier conduction band electron trapping and consequent longer electron-hole pair lifetimes.⁴¹

Conclusions

In summary, we have successfully synthesized Ag/TiO₂ heterojunctions with novel hierarchical architectures by a combination of an electrospinning method and a hydrothermal process. Moreover, the morphologies of secondary Ag nanoparticles size could be facily tuned by adjusting the experimental parameters. We believe this methodology provides a new avenue that offers a relatively mild and environmentally benign approach for large-scale preparation of various one-, two-, and three-dimensional heterojunctions with structural complexity and thus enable various functions. The special heterojunction possesses great potential for applications in photocatalysts, photovoltaics and supercapacitors in the future.

Acknowledgements

This work was financially supported by ChangChun Science and Technology plan projects (13NK01) and the National Nature Science Foundation (Grant 51403076).

Notes

^a College of Resources and Environment, Jilin Agriculture University, Changchun 130118, People's Republic of China

^b School of Aerospace Engineering, Tsinghua University, Beijing, 100000, China.

* Corresponding author E-mail: czq5974@163.com

[†] Electronic supplementary information (ESI) available.

[‡] Zhiqiang cheng and Fanli zhang contribute to the work equally.

References

- 1 A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37–38
- 2 Y. M. Lin, D. Z Li, J. H. Hu, G. C. Xiao, J. X. Wang, W. J. Li and X. Fu, *J. Phys. Chem. C*, 2012, **116**, 5764–5772.
- 3 J. Virkutyte, R. S. Varma, *RSC Advances*, 2012, **2**, 1533–1539
- 4 M. R. Elahifard, S. Rahimnejad, S. Haghghi and M. R. Gholami, *J. Am. Chem. Soc.*, 2007, **129**, 9552–9553
- 5 L. Z. Wang, T. Sasaki, *Chemical Reviews*, 2014, **114**, 9455
- 6 Y. Ohko I. Ando, C. Niwa, T. Tatsuma, T. Yamamura, T. Nakashima, Y. Kubota, and A. Fujishima, *Environ. Sci. Technol.*, 2001, **35**, 2365–2368.
- 7 U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissörtel, J. Salbeck, H. Spreitzer, M. Grätzel, *Nature*, 1998, **395**, 583–585
- 8 J. Gong, Y. Li, Z. Hu, Y. Deng, *Journal of Physical Chemistry C*, 2010, **114**, 9970–9974

- 9 H. T. Yu, X. Quan, S. Chen, H. M. Zhao, *Journal of Physical Chemistry C*, 2007, **111**, 12987-12991
- 10 S. Hoang, S. Guo, N. T. Hahn, A. J. Bard, C. B. Mullins, *Nano letters*, 2011, **12**, 26-32.
- 11 R. Mori, T. Ueta, K. Sakai, Y. Niida, Y. Koshiba, L. Lei, K. Nakamae, Y. Ueda, *Journal of materials science*, 2011, **46**, 1341-1350
- 12 A. L. Linsebigler, G. Q. Lu, J. T. Yates, *Chemical reviews*, 1995, **95**, 735-758
- 13 J. Yu, L. Qi, M. Jaroniec, *Journal of Physical Chemistry C*, 2010, **114**, 13118-13125
- 14 C. Y. Wang, D. W. Bahnemann, J. K. Dohrmann, *Chemical Communications*, 2000, **16**, 1539-1540
- 15 K. Yu, Y. Tian, T. Tatsuma, *Phys. Chem. Chem. Phys.*, 2006, **8**, 5417-5420.
- 16 C. M. Huang, G. T. Pan, Y. C. M. Li, M. H. Li, T. C. K. Yang, *Applied catalysis. A, General*, 2009, **358**, 164-172
- 17 Q. Xiang, J. Yu, M. Jaroniec, *Chemical Communications*, 2011, **47**, 4532-4534
- 18 X. Pan, M. Q. Yang, X. Fu, N. Zhang, Y. J. Xu, *Nanoscale*, 2013, **5**, 3601-3614
- 19 X. Zhou, G. Liu, J. Yu, W. Fan, *Journal of Materials Chemistry*, 2012, **22**, 21337-21354
- 20 F. Zhang, Z. Cheng, L. Kang, L. Cui, W. Liu, G. Hou, H. Yang, X. Xiao, *RSC advances.*, 2014, **4**, 63520-53525
- 21 J. Lu, F. Su, Z. Huang, C. Zhang, Y. Liu, X. Ma, J. Gong, *RSC Advances*, 2013, **3**, 720-724.
- 22 J. Lin, B. Ding, J. Yu, Y. Hsieh, *ACS applied materials & interfaces*, 2010, **2**, 521-528
- 23 D. Li, Y. Xia, *Nano Lett.*, 2003, **3**, 1167-1171
- 24 C. Su, L. Liu, M. Zhang, Y. Zhang and C. Shao, *CrystEngComm.*, 2012, **14**, 3989-3999
- 25 J. Y. Park, K. J. Hwang, J. W. Lee, I. H. Lee, *J Mater Sci.*, 2011, **46**, 7240-7246
- 26 Y. Yang, J. Wen, J. Wei, R. Xiong, J. Shi, C. Pan, *ACS applied materials & interfaces*, 2013, **5**, 6201-6207
- 27 Y. Bessekhoud, D. Robert and J. V. Weber, *J. Photochem. Photobiol., A*, 2004, **163**, 569-580
- 28 M. Y. Zhang, C. L. Shao, Z. C. Guo, Z. Y. Zhang, J. B. Mu, T. P. Cao and Y. C. Liu, *ACS Appl. Mater. Interfaces*, 2011, **3**, 369-377
- 29 M. Li, S. Zhang, Y. Peng, L. Lv, B. Pan, *RSC Advances*, 2015, **5**, 7363-7369
- 30 N. C. Jeong, C. Prasittichai, J. T. Hupp, *Langmuir*, 2011, **27**, 14609-14614
- 31 J. He, T. Kunitake, A. Nakao, *Chemistry of Materials*, 2003, **15**, 4401-4406
- 32 H. T. Ma, L. Qu, M. L. Huang, L. Y. Gu, N. Zhao, L. Wang, *Journal of Alloys and Compounds*, 2012, **537**, 286-290
- 33 P. L. Redmond, A. J. Hallock, L. E. Brus, *Nano letters*, 2005, **5**, 131-135
- 34 H. K. Irvani, S. V. Mirmohammadi, S. B. Zolfaghari, *Research in Pharmaceutical Sciences*, 2014, **9**, 385-406
- 35 X. B. Cao, X. M. Lan, Y. Guo, C. Zhao, S. M. Han, J. Wang and Q. R. Zhao, *J. Phys. Chem. C*, 2007, **111**, 18958-18964
- 36 J. D. Zhuang, W. X. Dai, Q. F. Tian, Z. H. Li, L. Y. Xie, J. X. Wang and P. Liu, *Langmuir*, 2010, **26**, 9686 - 9694
- 37 M. A. Behnajady, N. Modirshahla, M. Shokri, B. Rad, *Global Nest Journal*, 2008, **10**, 1-7
- 38 O. Carp, C. L. Huisman, A. Reller, *Progress in solid state chemistry*, 2004, **32**, 33-177
- 39 B. Xin, L. Jing, Z. Ren, B. Wang, H. Fu, *The Journal of Physical Chemistry B*, 2005, **109**, 2805-2809
- 40 N. Sobana, M. Muruganadham, M. Swaminathan, *Journal of Molecular Catalysis A: Chemical*, 2006, **258**, 124-132
- 41 Y. Wen, H. Ding, Y. Shan, *Nanoscale*, 2011, **3**, 4411-4417