

High Photocatalytic Activity of Hydrogen Production from Water Over Fe Doped and Ag Deposited Anatase TiO₂ Nanotube Arrays

Xiao Fan*, Jun Fan*, Xiaoyun Hu**, Enzhou Liu*, Limin Kang*, Chunni Tang*, Huitong Wu*, Yinye Li*, Yongning Ma*

*School of Chemical Engineering, Northwest University

No. 229 North Taibai Road, Xi'an, Shaanxi, P. R. China, fanjun@nwu.edu.cn;

**Department of Physics, Northwest University

No. 229 North Taibai Road, Xi'an, Shaanxi, P. R. China, hxy3275@nwu.edu.cn.

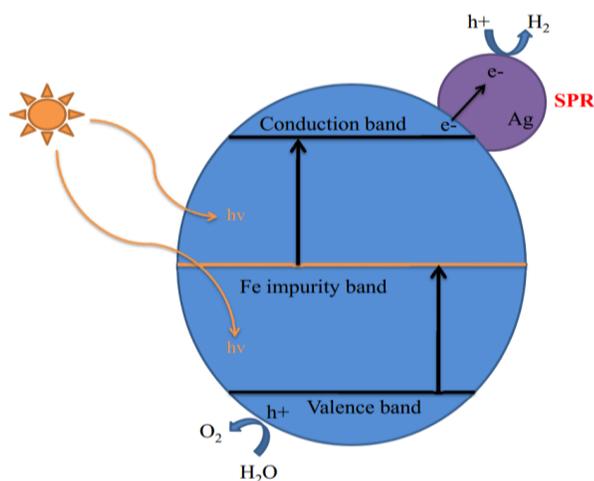
ABSTRACT

In this paper, Fe³⁺ ions doped anatase TiO₂ nanotube arrays (Fe/TiO₂ NTs) were successfully synthesized by the electrochemical anodic oxidation of pure titanium in an NH₄F electrolyte solution containing iron ions. Then Ag nanoparticles (Ag NPs) were assembled in Fe/TiO₂ nanotube arrays by microwave-assisted chemical reduction (Ag-Fe/TiO₂ NTs). The results indicated that Ag NPs were well dispersed on the surface of Fe/TiO₂ NTs, which can enhance the visible absorption of TiO₂ NTs based on the local surface plasmon resonance effect (LSPR) of Ag NPs. The photocatalytic activity of Ag-Fe/TiO₂ NTs was evaluated through the experiment of water splitting. At last, the mechanism of H₂ production by water splitting under visible light irradiation was also proposed.

effectiveness [1-4]. However, TiO₂ belongs to a wide band gap n-type semiconductor material (anatase for E_g= 3.2 eV) which can only harvest UV light. What's more, the high recombination rate of electron-hole pairs can also lead to its low photocatalytic efficiency.

Generally, noble metals, such as Pt, Au, and Ag are often applied to modify TiO₂ NTs for enhancing its H₂ production activity [5-7]. It is also proved to be an effective way to restrain the recombination of photo-generated electron-hole pairs. Furthermore, it should be noticed that doping with suitable transitional metals can also extend its light absorption to the visible spectrum and improve the separation efficiency of photo-induced electrons and holes [8-10].

In this work, Fe/TiO₂ NTs were successfully prepared by the electrochemical anodic oxidation of pure titanium in an NH₄F electrolyte solution containing iron ions. Then Noble metal Ag is employed to modify the Fe/TiO₂ NTs in this study. In addition, TiO₂ photocatalyst were applied to generate H₂ by water splitting to evaluate their photoactivity.



Keywords: localized surface plasmon resonance; nanotube arrays; Fe doped and Ag deposited; photocatalysis; water splitting

1 INTRODUCTION

Titanium dioxide (TiO₂) has been regarded as the most suitable catalyst for widespread environmental applications because of its biological and chemical properties, and cost-

2 EXPERIMENTAL

2.1 Preparation of the photocatalysts

Synthesis of Fe/TiO₂ NTs: Titanium sheets (>99% purity, 20×15 mm) were cleaned by sonication in acetone and deionized water. Then the cleaned Ti sheets were chemically etched in a mixture solution (HF-HNO₃-H₂O= 1:4:5 in v/v) for 5 min, followed by rinsing with deionized water and drying in air. A two-electrode system was applied with Ti foils as the working electrode and graphite as the counter electrode. The distance between the anode and cathode was 3 cm. Anodization was performed at 40 V for 6 h in 100 ml glycerol solution containing 0.3 wt% NH₄F and Fe(NO₃)₃ (0.1, 0.2 and 0.3 mM). The obtained TiO₂ nanotube arrays were annealed at 450 °C for 2 h with a heating rate of 5 °C/min.

Synthesis of Ag-Fe/TiO₂ NTs: Ag NPs were assembled in TiO₂ nanotube arrays by microwave-assisted chemical reduction. Microwave can support rapid, volumetric, and uniform heating, leading to enhanced structure and morphological properties for the nanomaterials. TiO₂ NTs

was immersed in 30 ml solution containing of AgNO_3 (0.1, 0.2 and 0.3 mM) and sodium citrate. Then the system was exposed to microwave irradiation for 5 min at 100 °C, and cooled to room temperature naturally. The microwave power was set at 300 W. Fe-Ag/TiO₂ NTs is obtained after cleaned and dried the resulting samples. The samples were donated as TiO₂ NTs, x mM Ag/ TiO₂ NTs, x mM Fe/TiO₂ NTs and x mM Fe-x mM Ag/TiO₂ NTs, respectively.

2.2 Characterization

The crystalline phase of samples was identified by Xray diffractometer (Shimadzu, XRD-6000, Cu K α radiation). The morphology was observed using a scanning electron microscope (SEM, JSM-6390A). The absorption property of samples was recorded using UV-vis spectrophotometer (Shimadzu, UV-3600). Raman spectra were collected on a Raman spectrometer (Renishaw inVia Reflex).

3 RESULTS AND DISCUSSION

Fig. 1 show SEM images of the samples. The TiO₂ NTs are orderly alined on the Ti substrate after anodization, with a diameter of approximately 120 nm, a well thickness of 30 nm. Ag NPs on the surface of Fe/TiO₂ NTs are obtained by microwave-assited reduction of AgNO_3 . The presence of Ag NPs does not damage the morphology of Fe/TiO₂ NTs. Most of Ag NPs are distributed on the exterior mouth of Fe/TiO₂ NTs. In top view, we can just observe the less amount of Ag NPs loaded on nanotubes.

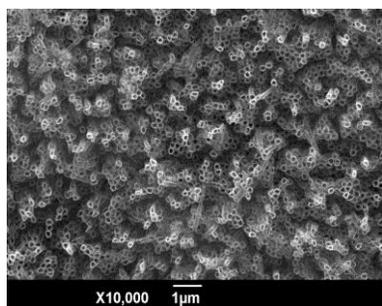
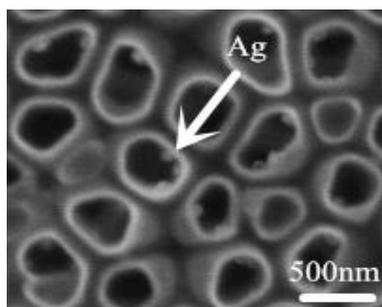


Fig.1 SEM images (a) pure TiO₂ NTs



(b) Fe doped and Ag NPs loaded on TiO₂ NTs

The XRD patterns of TiO₂ NTs and 0.2mMAg–0.3mMFe/TiO₂ NTs are showed in Fig. 2. The characteristic diffraction peaks of anatase TiO₂ are observed in all the samples, which are in good agreement with those in the standard JCPDS cards NO.21-1272. The loaded Ag NPs does not affect the crystal structure of TiO₂ NTs and the diffraction peaks of Ag NPs were not observed in Fig. 2, which may be related to the lower concentration of the AgNO_3 during the experiment. Due to the different atomic sizes of Fe³⁺ and Ti⁴⁺, some extent of deformation is introduced into the crystal lattice of TiO₂ [11]. Such a substitution not only lowers the crystallization of TiO₂, which is reflecter by a weaker diffraction intensity of XRD patten, but also slightly restrains the growth of TiO₂ crystallite [12].

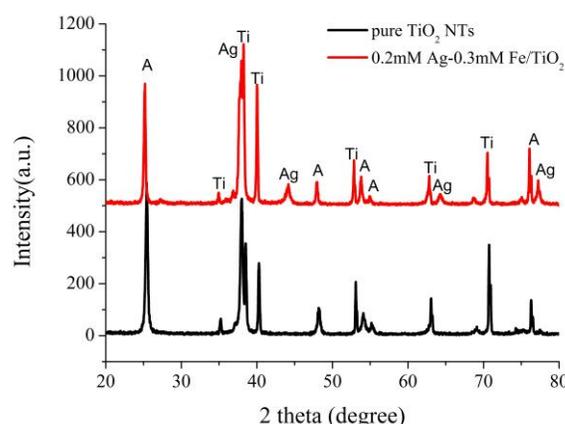


Fig. 2 XRD patterns of the prepared TiO₂ NTs

To investigate the optical properties of samples, the UV-vis absorption spectra were measured. As is shown in Fig. 3, all samples exhibit strong absorption in the range below 387 nm, comparing with pure TiO₂ NTs. In this work, the optimal value of Fe/Ti and Ag/Ti is 0.3 mM and 0.2 mM, respectively. Fe doped and Ag deposited TiO₂ samples display good visible light absorption activity and a clear red shift in the UV-visible light range. In all samples, 0.2mMAg–0.3mMFe/TiO₂ NTs shows the highest light harvesting activity from Fig. 3. All the samples doped with Fe³⁺ can result in the red shift of the UV-vis absorption spectra because of the d-d transition of Fe³⁺ (${}^2T_{2g} \rightarrow {}^2A_{2g}$, ${}^2T_{1g}$) or the charge transfer transition between interacting iron ions ($\text{Fe}^{3+} + \text{Fe}^{3+} \rightarrow \text{Fe}^{4+} + \text{Fe}^{2+}$) [13-14].

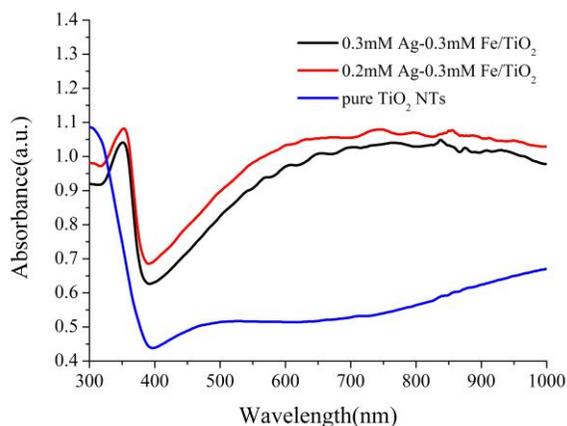


Fig. 3 UV-vis absorption spectra of the prepared TiO₂ NTs

Fig. 4 exhibits the photoluminescence (PL) emission spectrum of samples. PL emission spectrum is an important tool to study the efficiency of charge carrier trapping and transfer. PL emission mainly results from the recombination of excited electron-hole pairs, so it can be used to study the electron transfer between TiO₂ and Ag NPs [15]. The emission spectra of samples were recorded under 250 nm excitation. It can be observed clearly from Fig. 4 that their PL intensity of Ag-Fe/TiO₂ NTs is lower than that of pure TiO₂. Suitable values of Fe/Ti and Ag/Ti are separately to be 0.3 mM and 0.2 mM, which are in good accordance with Fig. 3. Furthermore, Fe-doped and Ag-deposited TiO₂ can further remarkably reduce PL intensity compared with those of single element modification. The above results indicate that the recombination of photo-generated electrons and holes is effectively suppressed by this method [16].

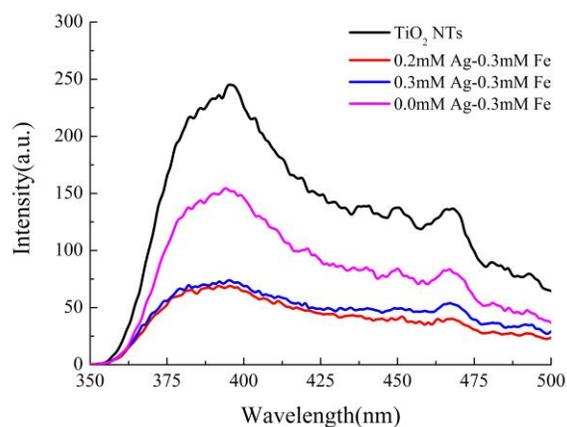


Fig. 4 Photoluminescence spectra of TiO₂ NTs under the excitation of 250 nm

Photocatalytic water splitting to generate hydrogen was used to evaluate the activity of catalyst using ethanol as a

sacrificial agent. In all cases, hydrogen evolves steadily over extended periods of time. It can be found that Ag-Fe/TiO₂ NTs samples performed better photocatalytic activity than pure TiO₂ NTs under UV light irradiation, which is 1.35 and 1.27 $\mu\text{mol}/(\text{cm}^2 \text{h})$, both higher than that of pure TiO₂ NTs under the same condition. This improvement results from the fact that the loaded Ag NPs and doped Fe ions restrained the recombination of electron-hole pairs [17].

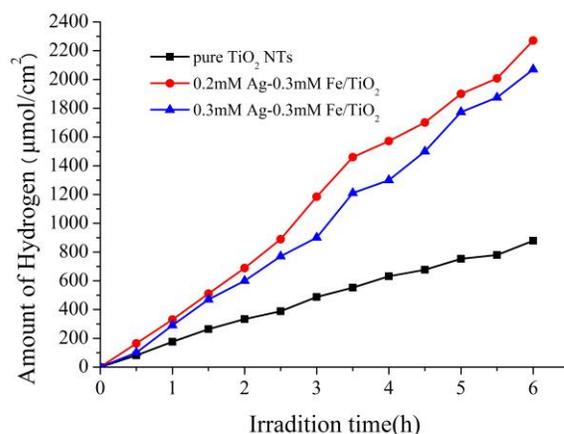


Fig. 5 H₂ production by water splitting over TiO₂ catalysts

4 CONCLUSIONS

Fe³⁺ ions doped anatase TiO₂ nanotube arrays were successfully synthesized by the electrochemical anodic oxidation of pure titanium in an NH₄F electrolyte solution containing iron ions and then Ag nanoparticles (Ag NPs) were assembled in Fe/TiO₂ nanotube arrays by microwave-assisted chemical reduction. The absorption of the samples was enhanced in the visible light based on the surface plasmon resonance effect of Ag NPs. In addition, Ag NPs could effectively restrain the recombination of photo-generated electron-hole pairs and the electron from the conduction band of TiO₂ to the metal surface. Fe³⁺ not only lowers the crystallization of TiO₂ but also slightly restrains the growth of TiO₂ crystallite. The experiment indicated that the hydrogen evolution rate of Ag-Fe/TiO₂ NTs samples irradiated by UV and visible light improved in various degrees compared with pure TiO₂.

5 ACKNOWLEDGEMENTS

This work supported by the National Natural Science Foundation of China (No. 21306150, No. 21176199 and No. 51372201), the Shaanxi Provincial Research Foundation for Basic Research, China (No. 2013JQ2003, No. 2011JM1001 and No. 2012JM1020), the Scientific Research and Industrialization Cultivation Foundations of Education Department of Shaanxi Provincial Government, China (No.

2013JK0693 and No. 2011JG05), the Scientific Research Foundation of Northwest University (No. 12NW19), and the Scientific Research Staring Foundation of Northwest University (No. PR12216).

REFERENCES

- [1] N. C. Jeong, C. Prasittichai, and J. T. Hupp, Photocurrent Enhancement by Surface Plasmon Resonance of Silver Nanoparticles in Highly Porous Dye-Sensitized Solar Cells, *Langmuir*, 27, 14609-14614, 2011.
- [2] Y. Hou, X. Y. Li, Q. D. Zhao, G. H. Chen, and C. L. Raston, Environmental Role of Hydroxyl Radicals and Mechanism of *Escherichia coli* Inactivation on Ag/AgBr/TiO₂ Nanotube Array Electrode under Visible Light Irradiation, *Science and Technology*, 46, 4042-4050, 2012.
- [3] Wang, Z.; Yang, C.; Lin, T.; Yin, H.; Chen, P.; Wan, D.; Xu, F.; Huang, F.; Lin, J.; Xie, X.; et al, H-doped Black Titania with Very High Solar Absorption and Excellent Photocatalysis Enhanced by Localized Surface Plasmon Resonance, *Adv. Funct. Mater.*, 23, 5444-5450, 2013.
- [4] J. J. Chen, J. C. S. Wu, P. C. Wu, and DP Tsai, Plasmonic Photocatalyst for H₂ Evolution in Photocatalytic Water Splitting, *Phys. Chem. C*, 115(1), 210-216, 2011.
- [5] A. Pearson, H. D. Zheng, K. Kalantar-zadeh, S. K. Bhargava and V. Bansal, Decoration of TiO₂ nanotubes with metal nano-particles using polyoxometalate as a uv-switable reducing agent for enhanced visible and solar light photocatalysis, *Langmuir*, 28(40), 14470-14475, 2012.
- [6] N. Zhang, S. Q. Liu, X. Z. Fu and Y. J. Xu, Synthesis of M@TiO₂ (M= Au, Pd, Pt) Core Shell Nanocomposites with Tunable Photoreactivity, *Physical Chemistry*, 115, 9136-9145, 2011.
- [7] S. T. Kochuveedu, D. P. Kim and D. H. Kim, Surface-Plasmon-Induced Visible Light Photocatalytic Activity of TiO₂ Nanospheres Decorated by Au Nanoparticles with Controlled Configuration, *Physical Chemistry*, 116, 2500-2506, 2012.
- [8] L. G. Devil, B. Nagaraj, K. E. Rajashekhar, Synergistic effect of Ag deposition and nitrogen doping in TiO₂ for the degradation of phenol under solar irradiation in presence of electron acceptor, *Chem. Eng. J.*, 181-182, 259-266, 2012.
- [9] L. F. Liu, F. Chen, F. L. Yang, Y. S. Chen, J. Crittenden, Photocatalytic degradation of 2,4-dichlorophenol using nanoscale Fe/TiO₂, *Chem. Eng. J.*, 181-182, 189-195, 2012.
- [10] W. Ji, Y. Kitahama, X. Xue, B. Zhao and Y. Ozaki, Generation of Pronounced Resonance Profile of Charge-Transfer Contributions to Surface-Enhanced Raman Scattering, *Phys. Chem. C*, 116, 2515-2520, 2012.
- [11] Y. Lu, H. T. Yu, S. Chen, X. Quan and H. M. Zhao, Integrating Plasmonic Nanoparticles with TiO₂ Photonic Crystal for Enhancement of Visible-Light-Driven Photocatalysis, *Environ. Sci. Technol.*, 46, 1724-1730, 2012.
- [12] Xiao F, An efficient layer-by-layer self-assembly of metal-TiO₂ nanoring/nanotube heterostructures, M/T-NRNT (M= Au, Ag, Pt), for versatile catalytic application, *Chem. Commun.*, 48, 6538-6540, 2012.
- [13] P. Christopher, D. B. Ingram and S. Linic, Enhancing Photochemical activity of semiconductor nanoparticles with optical active Ag nanostructures: Photochemistry Mediated by Ag Surface Plasmons, *Phys. Chem. C*, 114, 9173-9177, 2010.
- [14] Kochuveedu S T, Kim D P, Kim D H. Surface-plasmon-induced visible light photocatalytic activity of TiO₂ nanospheres decorated by Au nanoparticles with controlled configuration, *The Journal of Physical Chemistry C*, 116, 2500-2506, 2012.
- [15] Zhai W, Xue S, Zhu A, et al. Plasmon - driven selective oxidation of aromatic alcohols to aldehydes in water with recyclable Pt/TiO₂ nanocomposites, *Chem. Cat. Chem*, 3, 127-130, 2011.
- [16] Kar P, Banerjee T, Verma S, et al. Photosensitization of nanoparticulate TiO₂ using a Re (i)-polypyridyl complex: studies on interfacial electron transfer in the ultrafast time domain, *Physical Chemistry Chemical Physics*, 14, 8192-8198, 2012.
- [17] Jing L, Zhou J, Durrant J R, et al. Dynamics of photogenerated charges in the phosphate modified TiO₂ and the enhanced activity for photoelectrochemical water splitting, *Energy Environ. Sci.*, 5, 6552-6558, 2012.