

# Au Nanoparticles Decorated Hydrothermally Processed Rutile TiO<sub>2</sub> Nanorods for Photoelectrochemical Water Splitting

Bo Sun, Tielin Shi, Wenjun Sheng, Ting Jiang and Guanglan Liao\*

State Key Laboratory of Digital Manufacturing Equipment and Technology, Huazhong University of Science and Technology, Wuhan 430074, China

bosun@hust.edu.cn, tlshi@hust.edu.cn, coraldevil@hust.edu.cn, jiangting@hust.edu.cn, guanglan.liao@hust.edu.cn.

## ABSTRACT

In this work, we investigate the synthesis of single crystalline rutile TiO<sub>2</sub> nanorods for photoelectrochemical water splitting. A facile and convenient hydrothermal process was used, and we realize the control of the length, diameter and density of the nanorods on transparent conductive fluorine-doped tin oxide substrates by varying the growth parameters. To investigate the influence of the substrate we also replace the substrate with silicon and common glass, and the effect of the growing time is discussed as well. Besides, we decorate the nanorods with Au nanoparticles to improve the catalytic activity. Under the illumination from solar simulator, the Au nanoparticles decorated TiO<sub>2</sub> nanorods film produces a photocurrent density of 0.52 mA/cm<sup>2</sup> at 0V versus the reference electrode.

**Keywords:** Au nanoparticles, rutile, TiO<sub>2</sub> nanorods, photoelectrochemical, water splitting.

## 1 INTRODUCTION

Since the first report of the photoelectrochemical water splitting using n-type TiO<sub>2</sub> in 1972<sup>[1]</sup>, TiO<sub>2</sub> has aroused more and more attentions and is considered as one of the most promising materials as photoelectrode for solar water splitting, because of its high chemical stability, low cost and nontoxicity<sup>[2,3]</sup>.

Early efforts mainly focus on the nanoparticles films for their large surface area to volume ratios. However, the high charge carrier recombination and low electron mobility at the grain boundary limit the performance of the films<sup>[4,5]</sup>. Recently, researches concentrated on the one dimensional nanostructure including nanorods<sup>[6-8]</sup>, nanotubes<sup>[9-11]</sup> and nanowires<sup>[12-13]</sup>. Various fabrication process were developed for the synthesis of TiO<sub>2</sub> nanorods, nanowires or nanotubes, such as catalyst-assisted vapor-liquid-solid (VLS)<sup>[12]</sup>, hydrothermal process<sup>[14]</sup>, electrochemical anodization<sup>[15-16]</sup>, etc. However, TiO<sub>2</sub> is a wide band gap semiconductor only absorbing UV-light, which suppress further applications. Considerable effort have been devoted to improve the photon absorption and photocatalytic efficiency of TiO<sub>2</sub> nanostructures, such as synthesizing branched structures<sup>[17]</sup>, adjusting its crystallite

size and structure<sup>[18]</sup>, exposing the activity surface<sup>[19]</sup>, doping with other elements to tune the bandgap<sup>[20-21]</sup>, and sensitizing with other small bandgap semiconductor materials such as PbS<sup>[10]</sup>, CdSe<sup>[22]</sup>, CuInS<sup>[23]</sup>, and hydrogen annealing process<sup>[24]</sup>.

In this paper, we introduce a convenient method suitable for mass fabrication, decorating the TiO<sub>2</sub> nanorods with Au nanoparticles. This approach can greatly improve the visible light absorbance and the water splitting performance.

## 2 EXPERIMENTAL PROCEDURES

In the experiments, the transparent conductive fluorine-doped tin oxide (FTO) glass was ultrasonically cleaned in the mixed solution of deionized (DI) water, acetone and ethanol for 30min (the volume ratio 1:1:1). Then 30mL DI water was mixed with 30 mL hydrochloric acid in a Teflon-lined stainless steel autoclave. The mixture was stirred for 5 min before adding 1 mL tetrabutyl titanate. After another 5 min stir the cleaned FTO substrate was placed into the Teflon-liner with the conducting side facing down. The synthesis process was conducted at 150°C or 180°C for 6-22 h in an electric oven. After that the autoclave was cooled by flowing water, and the FTO substrate was taken out and rinsed with deionized water. Finally, the samples were annealed at 450°C for 2 h in the air.

In order to investigate the influence of the substrate, we replaced the FTO substrate with the silicon wafer and common glass for comparison. Besides, we decorated the nanorods with Au nanoparticles to improve the catalytic activity. The Au nanoparticles were coated on the nanorods by magnetic sputtering.

The morphology and lattice structure of the nanorods film was examined with the field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM), while the crystal structure was examined with X-ray diffraction (XRD). We detached the white film from the FTO substrate with a blade and then added the film into ethanol followed by sonication for about 20 min. Two drops of the sonicated solution were dropped onto the copper grid and dried by heating in the ambient air for TEM imaging. The light absorption of the film was characterized with an ultraviolet spectrophotometer.

For photoelectrochemical (PEC) water splitting performance measurement, the exposed FTO was covered

with a layer of silver and connected to Cu wires with solder. Then, the electrode, edge and some part of the film were sealed with Polydimethylsiloxane (PDMS) or epoxy, only a well-defined area of the white film being exposed to the electrolyte. A common glass vessel filled with 400 mL 1M KOH was used as the PEC cell, and a class AAA solar simulator (Newport oriel 94043A) was used as light source. Besides, a Pt slice as the counter electrode and an Ag/AgCl reference electrode was used for the PEC measurement.

### 3 RESULTS AND DISCUSSIONS

The XRD patterns of the TiO<sub>2</sub> nanorods on FTO and silicon are displayed in Fig. 1. All the diffraction peaks agree well with the tetragonal rutile TiO<sub>2</sub> phase, indicating that we have obtained single crystalline rutile TiO<sub>2</sub> nanorods, as shown in Fig. 2 and Fig. 3. The uniform aligned rutile TiO<sub>2</sub> nanorods on the FTO substrate are displayed in Fig. 2. The nanorods with the diameter about 50nm in Fig. 2(a) and 2(b) were synthesized at 180 °C for 5 h, while the nanorods in Fig. 2(c) and 2(d) with the diameter about 200 nm were synthesized at 150 °C for 18 h. The inset is an optical photo of the nanorods film on FTO glass. It is obvious that the length of the nanorods are both 2 μm or so and there is almost no difference between Fig. 2(b) and 2(d), while the diameters are significantly different. The reason for this phenomenon is that high temperature may increase the growth rate along the nanorods greatly, but the effect on the growth perpendicular to the nanorods is slightly. Also, we can find that the diameter depends greatly on the reaction time, 5 h for 50 nm and 18 h for 200 nm..

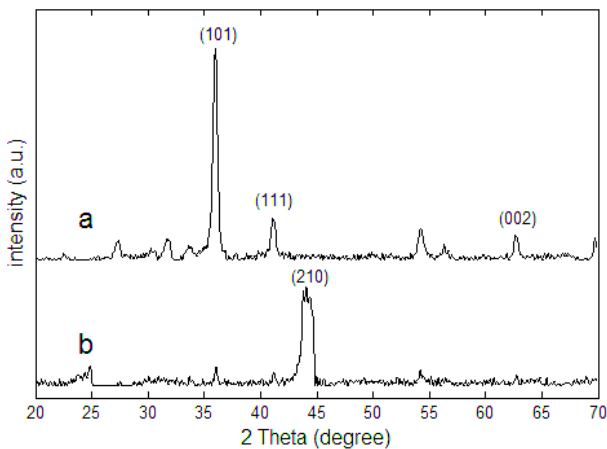


Fig. 1. XRD patterns of the TiO<sub>2</sub> nanorods on different substrates: (a) FTO, (b) silicon.

To investigate the influences of the substrates, we replaced the FTO substrate with the silicon wafer and conducted the process at 150 °C for 4, 10 and 20 h, respectively. The results are depicted in Fig. 3. We can find only some isolated nanoparticles with the size about 500

nm exist on the silicon after 4 h growth, as shown in Fig. 3(a). After 10 h growth there appear flower-like nanorods cluster with the diameter about 200 nm and the length about 2 μm. After that the clusters turn larger further for growing 20 h as shown in Fig. 3(c) and 3(d).

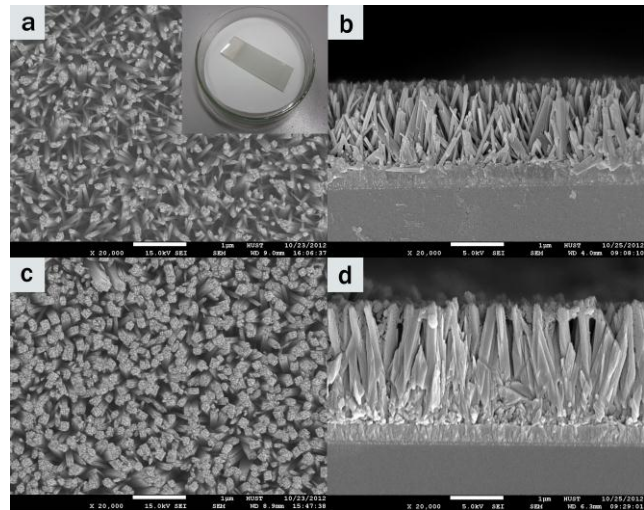


Fig. 2. TiO<sub>2</sub> nanorods growth on FTO at different conditions: (a) and (b) 180 °C, 5 h; (c) and (d) 150 °C, 18 h. The inset is an optical photo.

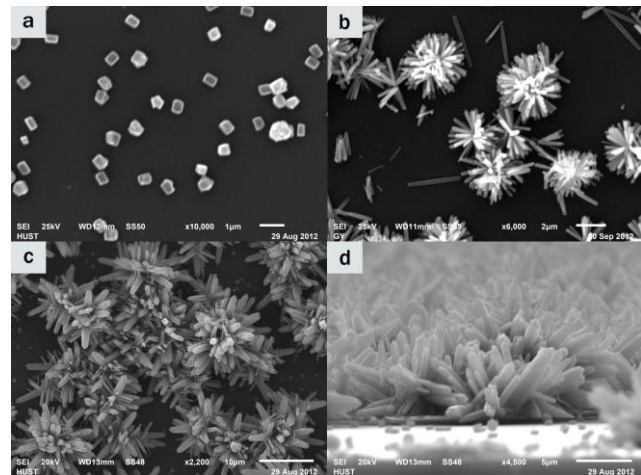


Fig. 3. TiO<sub>2</sub> nanorods growth on silicon at 150 °C for different times, (a) 4 h, (b) 10 h, (c) and (d) 20 h.

In the experiments, we need to emphasize that the nanorods cluster don't contact well with the silicon substrate. The white film may be detached from the silicon substrate even just under the rapid flowing water. We also replaced the FTO substrate with common used glass. There is nothing growing on the glass. On the contrary, the nanorods can be attached firmly to the FTO substrate, and couldn't be detached even with the aid of ultrasonication. It means that the nucleation and growth may require epitaxy on FTO crystals. In fact, the lattice mismatch between the

rutile  $\text{TiO}_2$  and FTO is very small, which may promote the epitaxial nucleation and growth of rutile  $\text{TiO}_2$  nanorods.

Increasing the surface area is a widely accepted route to improve the PEC performance. We once try to increase the length by prolonging the reaction time. However, when the reaction time exceeds 24 h under  $150^\circ\text{C}$ , the  $\text{TiO}_2$  film will peel off the substrate automatically. The peeling of the film may be caused by the competition between the crystal growth and dissolution. At the beginning, the supersaturation of the titanium salt is high and the nanorods grow quickly. Then the growth will decrease as the concentration of the titanium salt decrease. When the system approaches to equilibrium, the dissolution of high-energy surfaces become serious, especially for the  $\text{TiO}_2$  and FTO contact surface. Thus, the nanorods can not attach well with the substrate after a long time growth. However, the peeled off white film can easily be collected by a tweezer and transferred to other substrate while maintaining its microscopic structure. This may provides some new applications of the  $\text{TiO}_2$  nanorods. At last, we repeated the process to obtain the nanorods with longer length as shown in Fig. 4. The nanorods film depicted in Fig. 4(a) was synthesized at  $180^\circ\text{C}$  for 6 h, and Fig. 4(b) display the nanorods obtained by two step reactions: the FTO substrate was placed into the Teflon-liner for the first the reaction at  $180^\circ\text{C}$  for 6 h, then the sample was taken out and rinsed, after that the sample was place into another Teflon-liner filled with fresh reaction solution for the second step reaction at  $180^\circ\text{C}$  for 6 h.

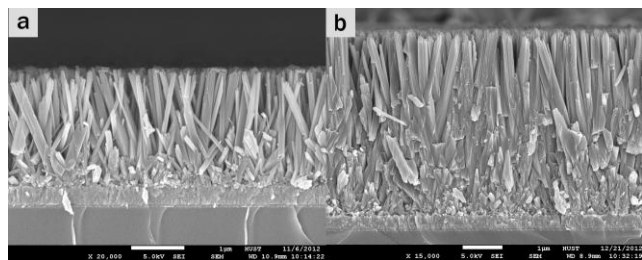


Fig. 4. The nanorods obtained: (a) after the reaction at  $180^\circ\text{C}$  for 6 h, (b) after the two step reactions.

Fig. 5 displays the TEM and HRTEM images of  $\text{TiO}_2$  nanorods before and after the decoration with Au nanoparticles. Fig. 5(a) illustrates the structure of a single nanorod, indicating that the nanorod composites of nano-bundle. The HRTEM image of the nanorods edge is shown in Fig. 5(b), where we can find a single crystalline structure clearly. Fig. 5(c) is the TEM image of the nanorod with Au nanoparticles. It is obvious that the Au nanoparticles is also single crystalline structure as shown in Fig. 5(d).

The Fig. 6 depicted the light absorption of the  $\text{TiO}_2$  nanorods film on FTO substrate before and after Au nanoparticles decoration, where the inset is the optical image of the samples. Obviously, the light absorption of the nanorods with Au nanoparticles is better, especially for the visible light region. Besides, we can find clearly that there

is an absorption peak on the curve at 550 nm. This may be caused by the Plasma resonance effect. Corresponding to the absorption curve, the pure  $\text{TiO}_2$  nanorods film shows the white color since it just absorb the UV-light, while the Au- $\text{TiO}_2$  nanorods film is kermesinus, because its absorption of red light is slightly lower than others. This agrees well with the absorption curve as we can see that the absorption begin to decrease after 550 nm.

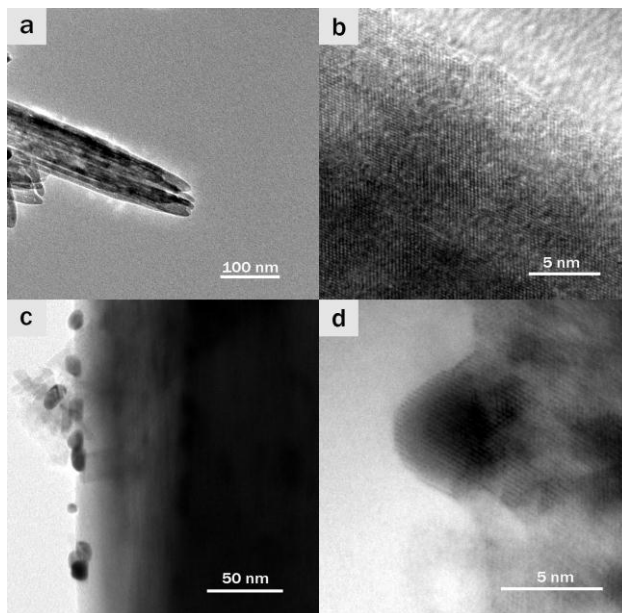


Fig. 5. TEM and HRTEM images of the  $\text{TiO}_2$  nanorods and Au decorated  $\text{TiO}_2$  nanorods: (a) TEM image of a single  $\text{TiO}_2$  nanorod, (b) HRTEM image of the single nanorod edge, (c) TEM image of a Au nanoparticles decorated  $\text{TiO}_2$  nanorod, (d) HRTEM image of the Au nanoparticles.

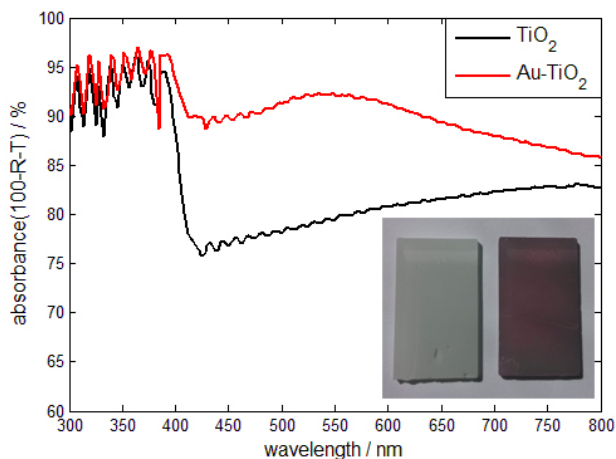


Fig. 6. Light absorption of the rutile  $\text{TiO}_2$  nanorods films on FTO substrates with and without Au nanoparticles.

To study the photoelectrochemical water splitting performance of the nanorods films further, the naorods with

length about  $2.2\mu\text{m}$  was packaged. The photocurrent density versus the potential (J-V) curves under the illumination of class AAA solar simulator ( $100\text{mW}/\text{cm}^2$ ) were measured, as shown in Fig.7. It is obviously that the performance of nanorods decorated with 5-10 nm Au nanoparticles is better than those without Au nanoparticles. The photocurrent density has reached to  $0.52\text{ mA}/\text{cm}^2$  at 0 V versus the reference electrode and can be improved by further optimization.

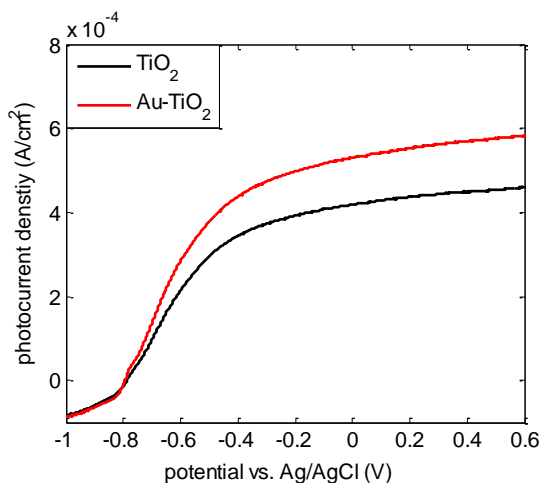


Fig. 7. Lineal sweep voltammograms of the rutile  $\text{TiO}_2$  nanorods films on FTO substrates with and without Au nanoparticles.

## 4 CONCLUSION

In summary, we have realized the controlled synthesis of the uniform rutile  $\text{TiO}_2$  nanorods on FTO substrate.  $\text{TiO}_2$  nanorods with different diameter, length, density can be obtained by tuning the react parameters. Besides, we have achieved the synthesis of clustered  $\text{TiO}_2$  nanorods on silicon wafer, and discussed the influence of the substrate. A lattice structure mismatch hypothesis have been proposed to explain the detaching or peeling off of the  $\text{TiO}_2$  film. To improve the photocatalytic activity, we decorated the  $\text{TiO}_2$  nanorods with Au nanoparticles. The light absorption in the experiments have proved the benefits of the Au nanoparticles. At last, the PEC performance of the pure  $\text{TiO}_2$  nanorods film and the  $\text{Au-TiO}_2$  nanorods film were tested. It is obvious that the Au nanoparticles can greatly enhance the photocatalytic activity, and can be used to improve the water splitting efficiency.

## ACKNOWLEDGEMENTS

The authors are grateful for the financial supports by National Key Basic Research Special Fund of China (Grant No. 2009CB724204) and National Natural Science Foundation of China (Grant Nos. 51175210 and 51222508).

## REFERENCES

- [1] A. Fujishima, K. Honda, *Nature* 238, 37, 1972.
- [2] P. Roy, S. Berger, P. Schmuki, *Angew. Chem. Int. Ed.* 50, 2904, 2011.
- [3] T. Bak, J. Nowotny, M. Rekas, C. C. Sorrell, *Int. J. Hydrog. Energy* 27, 991, 2002.
- [4] E. Hendry, M. Koeberg, B. O'Regan, M. Bonn, *Nano Lett.* 6, 755, 2006.
- [5] E. Yagi, R. R. Hasiguti, M. Aono, *Phys. Rev. B* 54, 7945, 1996.
- [6] J. H. Bang, P. V. Kamat, *Adv. Funct. Mater.* 20, 1970, 2010.
- [7] X. J. Feng, K. Shankar, O. K. Varghese, M. Paulose, T. J. Latempa, C. A. Grimes, *Nano Lett.* 8, 3781, 2008.
- [8] J. K. Oh, J. K. Lee, H. S. Kim, S. B. Han, K. W. Park, *Chem. Mater.* 22, 1114, 2010.
- [9] Z. H. Zhang, M. F. Hossain, T. Takahashi, *Int. J. Hydrog. Energy* 35, 8528, 2010.
- [10] C. Ratanatawanate, C. R. Xiong, K. J. Balkus, Jr. *ACS Nano* 2, 1682, 2008.
- [11] Y. Hou, X. Y. Li, Q. D. Zhao, X. Quana, G. H. Chen, *J. Mater. Chem.* 21, 18067, 2011.
- [12] Yi-Seul Park and Jin Seok Lee, *Bull. Korean Chem. Soc.* 32, 3571, 2011.
- [13] J. Z. Chen, W. Y. Ko, Y. C. Yen, P. H. Chen, K. J. Lin, *ACS Nano* 6, 6633, 2012.
- [14] B. Liu, E. S. Aydil, *J. Am. Chem. Soc.* 131, 3985, 2009.
- [15] S. P. Albu, A. Ghicov, J. M. Macak, P. Schmuki, *Phys. Status Solidi RRL*, 1, R65, 2007.
- [16] I. Paramasivam, J. M. Macak, T. Selvam, P. Schmuki, *Electrochim. Acta* 54, 643, 2008.
- [17] I. S. Cho, Z. B. Chen, A. J. Forman, D. R. Kim, P. M. Rao, T. F. Jaramillo, X. L. Zheng, *Nano Lett.* 11, 4978, 2011.
- [18] P. Roy, S. Berger, P. Schmuki, *Angew. Chem., Int. Ed.* 50, 2904, 2011.
- [19] X. L. Liu, H. M. Zhang, X. D. Yao, T. C. An, P. R. Liu, Y. Wang, F. Peng, A. R. Carroll, H. J. Zhao, *Nano Research* 5, 762, 2012.
- [20] S. Hoang, S. Guo, N. T. Hahn, A. J. Bard, C. B. Mullins, *Nano Lett.* 12, 26, 2012.
- [21] M. Xu, P. M. Da, H. Y. Wu, D. Y. Zhao, G. F. Zheng, *Nano Lett.* 12, 1503, 2012.
- [22] J. H. Bang, P. V. Kamat, *Adv. Funct. Mater.* 20, 1970, 2010.
- [23] Z. J. Zhou, S. J. Yuan, J. Q. Fan, Z. L. Hou, W. H. Zhou, Z. L. Du, S. X. Wu, *Nanoscale Research Letters* 7, 652, 2012.
- [24] G. M. Wang, H. Y. Wang, Y. C. Ling, Y. C. Tang, X. Y. Yang, R. C. Fitzmorris, C. C. Wang, J. Z. Zhang, Y. Li, *Nano Lett.* 11, 3026, 2011.