



# Photoelectric properties of cystine-modified nano-TiO<sub>2</sub> with visible-light response

Xiu-Wen Cheng<sup>a,b,c</sup>, Xiu-Juan Yu<sup>a,\*</sup>, Zipeng Xing<sup>a</sup>

<sup>a</sup> Department of Environmental Science and Engineering, Heilongjiang University, Xuefu Road 74, Nangang District, Harbin 150080, Heilongjiang Province, PR China

<sup>b</sup> State Key Laboratory of Urban Water Resources and Environment, Harbin Institute of Technology, Huanghe Road 73, Nangang District, Harbin 150090, PR China

<sup>c</sup> Department of Environmental Science and Engineering, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Huanghe Road 73, Nangang District, Harbin 150090, PR China

## ARTICLE INFO

### Article history:

Received 27 October 2011

Received in revised form 7 January 2012

Accepted 24 January 2012

Available online 2 February 2012

### Keywords:

Cystine

TiO<sub>2</sub>

Visible-light

Photoelectric properties

## ABSTRACT

Visible light responsible TiO<sub>2</sub> nano-particles (TiO<sub>2</sub> NPs) were prepared through sol-gel method using tetrabutyl titanate and biomolecule cystine as raw materials. The resulting materials were characterized by X-ray diffraction (XRD), ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS), surface photovoltage spectroscopy (SPS) and electric field induced surface photovoltage spectroscopy (EFISPS). The XRD results showed that the addition of cystine could effectively retard the phase transformation of TiO<sub>2</sub> from anatase to rutile and the growth of crystallite sizes. DRS results indicated that the light absorption edge of TiO<sub>2</sub> was significantly red-shifted to visible region with the addition of biomolecule cystine. SPS results exhibited that the separation efficiency of the photoinduced charge carriers of TiO<sub>2</sub> were effectively improved. In addition, EFISPS indicated that TiO<sub>2</sub> nano-particles modification with biomolecule cystine were still n-type semiconductor.

Crown Copyright © 2012 Published by Elsevier B.V. All rights reserved.

## 1. Introduction

Recently, titanium dioxide (TiO<sub>2</sub>) photocatalysis has been considered as a promising technology for the air purification, solar energy conversion and waste water treatment [1–4]. However, pure TiO<sub>2</sub> due to its wide band gap (anatase 3.2 eV) can only be excited by UV light, which only accounts for a small part of the solar spectrum [5]. Thus, how to make full use of the solar energy has been the current key research aspect. In 2001, Asahi et al. [6] reported that TiO<sub>2</sub> doped with nitrogen could improve the photoresponse and visible light photocatalytic activity. From then on, a great deal of efforts has been made, such as dye sensitization, noble metal deposition, coupling of TiO<sub>2</sub> with a narrow semiconductor and doping of TiO<sub>2</sub> with foreign ions [7–11]. Among which, doping of TiO<sub>2</sub> with non-metal element has been considered as the most feasible and effective approach to improved the visible light photoresponse and photocatalytic activity. Nevertheless, the current dominating research has mainly focused on the preparing technique and doping species for the synthesis of visible light responsible TiO<sub>2</sub>, while to the systematic investigation for the photoelectric property has rarely been reported. As we known, doping of TiO<sub>2</sub> with foreign ions depend, to some extent, on ions sources.

Thus, the selection of ion sources is crucial for the synthesis of non-metal-ion-doped catalyst with high photocatalytic activity.

Cystine is a biomolecule which consists primarily of carbon, hydrogen and oxygen, along with nitrogen and sulfur. Recently, biomolecule-controlled/assisted synthesis methods have become a new and promising focus on the preparation of various nano-materials due to their attracting structure and self-assembling role of biomolecules. However, to the best of our knowledge, systematic studies on TiO<sub>2</sub> modified by cystine, together with their relationship with the photoelectric activity has never been reported so far.

In this study, biomolecule cystine modified TiO<sub>2</sub> nano-particles were synthesized through sol-gel method using tetrabutyl titanate and cystine as raw materials. The phase transformation of TiO<sub>2</sub> from anatase to rutile and the growth of crystallite sizes have been effectively inhibited. In addition, the light absorption in visible region and separation efficiency of photoinduced charge carriers of TiO<sub>2</sub> were greatly improved by modifying with a certain amount of biomolecule cystine.

## 2. Experimental

### 2.1. Synthesis of materials

Typically, a solution consisting of 10 mL absolute ethanol, 12 mL dilute nitric acid (1:5, v/v between concentrated nitric acid and deionized water) and a certain amount of cystine was added dropwise into a solution containing of 40 mL absolute ethanol and 10 mL tetrabutyl titanate within 120 min under vigorous stirring. After

\* Corresponding author. Tel.: +86 451 86608549; fax: +86 451 86413259.  
E-mail address: [yuxjuan@hit.edu.cn](mailto:yuxjuan@hit.edu.cn) (X.-J. Yu).

being aged for 6 h at room temperature, the wet gel was dried at 353 K for 36 h in an oven. Subsequently, the TiO<sub>2</sub> xerogel was calcined at 623 K for 4 h in air condition. Finally, the cystine modified TiO<sub>2</sub> samples were successfully obtained by grinding the calcined xerogel. The molar percent of cystine to TiO<sub>2</sub>, hereafter denoted by *R*, was equal to 0, 3.3, 4.2, 7.1 and 10, and the corresponding samples were labeled as R0, R3.3, R4.2, R7.1 and R10, respectively.

## 2.2. Characterization of materials

X-ray diffraction (XRD) patterns were performed on Model D/MAX-IIIIB diffractometer equipped with Cu K<sub>α</sub> radiation source ( $\lambda = 1.5418 \text{ \AA}$ ). An accelerating voltage of 40 kV and an emission current of 30 mA were employed, respectively. UV–vis diffuse reflectance spectra (UV–vis DRS) of the samples were conducted on a UV–vis spectrophotometer (UV-2550, Shimadzu) with an integrating sphere attachment, and BaSO<sub>4</sub> was used as the reference material. Surface photovoltage spectra (SPS) measurements were carried out with a home-built apparatus described elsewhere, and the powder samples were sandwiched between two ITO glass electrodes [12,13].

## 3. Results and discussion

### 3.1. XRD analysis

Fig. 1 showed the XRD patterns of TiO<sub>2</sub> modified with different amount of cystine. Clearly, pure TiO<sub>2</sub> contained anatase (JCPDS, No. 21-1272), rutile (JCPDS, No. 21-1276) and brookite (JCPDS, No. 29-1360) with anatase phase in the majority according to their peak intensities. However, cystine modified TiO<sub>2</sub> samples did not show any additional phase except anatase. Generally, brookite is a transitional phase from anatase to rutile during the calcinating process. Thus, it can be concluded that modification with cystine could effective inhibit the phase transformation of TiO<sub>2</sub> from anatase to rutile. It is noteworthy that the crystallinity was greatly decreased by modifying with biomolecule cystine, which may be caused from the doping species. Further, the average crystallite sizes of the as-synthesized samples can be calculated by applying the Debye–Scherrer formula [14] on the anatase (1 0 1) diffraction peaks:

$$d = \frac{K\lambda}{\beta \cos \theta}$$

where *d* is the crystallite size,  $\lambda$  is the wavelength of X-ray radiation (in our test,  $\lambda = 0.15418 \text{ nm}$ ), *K* is a constant ( $K = 0.89$ );  $\beta$  is the full width at half-maximum;  $\theta$  is the diffraction angle. After calculating, the crystallite sizes of R0, R3.3, R4.2, R5.0, R7.1 and R10 were found to be 6.9, 5.4, 5.26, 5.45, 5.56 and 5.67 nm, respectively. Therefore, it can be induced that modification with cystine could inhibit the growth of crystallite size of TiO<sub>2</sub>. Besides these, as the additional amount of cystine increased, the crystallite size decreased

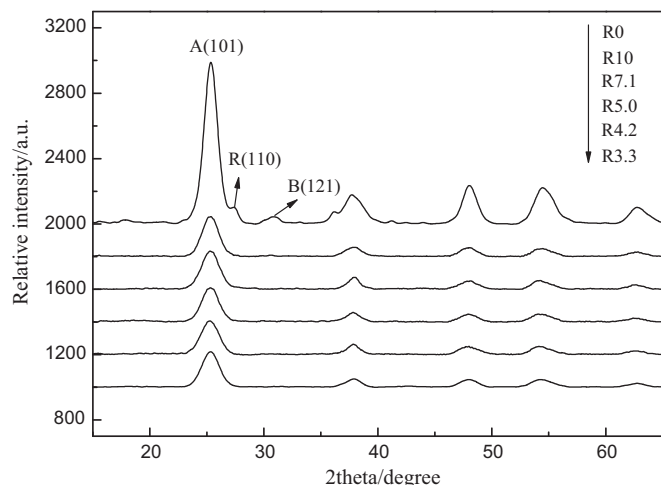


Fig. 1. XRD patterns of different TiO<sub>2</sub> photocatalysts.

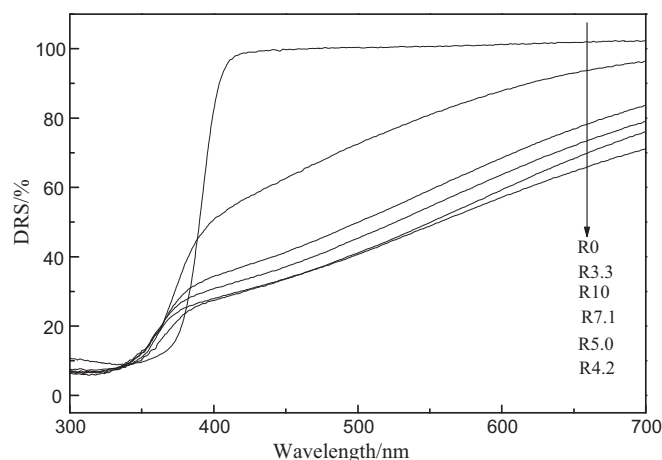


Fig. 2. UV–vis DRS spectra of different TiO<sub>2</sub> photocatalysts.

inversely. When the additional cystine content was 4.2%, the R4.2 sample exhibited smallest crystallite size. If the cystine content continuously increased, the crystallite size began to increase.

### 3.2. DRS analysis

In order to investigate the optical property of the as-synthesized TiO<sub>2</sub> nano-particles, UV–vis DRS spectra had been measured and shown in Fig. 2. As displayed in Fig. 2, after modification with cystine, the light absorption edge of TiO<sub>2</sub> was significantly red shifted to visible region, which was attributed to the non-metal doping. As non-metal was incorporated into the lattice of TiO<sub>2</sub>, a new energy level was introduced. Therefore, the visible light photoresponse was greatly improved, which could enhance the visible light photocatalytic activity. When the additional amount of cystine was 4.2%, the R4.2 sample exhibited the strongest light absorption in visible region, suggesting that it should possess highest photocatalytic activity for the degradation of organic pollutants. If the cystine content continuously increased, the light absorption in visible region began to go down inversely, indicating that controlling the addition of biomolecule cystine was crucial to obtain an optimal optical property of TiO<sub>2</sub>.

### 3.3. SPS analysis

The surface photovoltage generation mainly arises from the creation of electron/hole pairs, followed by the separation under a built-in electric field (also called space-charge layer). Thus, it can be expected that the stronger the surface photovoltage spectroscopy (SPS) response is, the higher separation efficiency the photoinduced charge carriers is [15]. Fig. 3 showed the SPS responses of TiO<sub>2</sub> samples modification with different amount of biomolecule cystine. For all the samples, an obvious SPS response can be obvious found at the wavelength range from 300 to 370 nm, which was attributed to the electron transitions from the valence band to conduction band (O2p → Ti3d) on the basis of the DRS spectra and TiO<sub>2</sub> band structure [11,15]. As the cystine amount increased, the SPS responses became strong. When the cystine content was 4.2%, the highest SPS response appeared. However, after continuously increasing cystine amount, the SPS response began to become weak inversely, indicating that modification with an appropriate amount of cystine can greatly enhance the SPS response of TiO<sub>2</sub> so as to promote the separation efficiency of photoinduced charge carriers, which was possibly attributed to non-metal doping. When the non-metal was doped into the lattice of TiO<sub>2</sub>, a new impurity level was formed between the valence band and the conduction band, which greatly

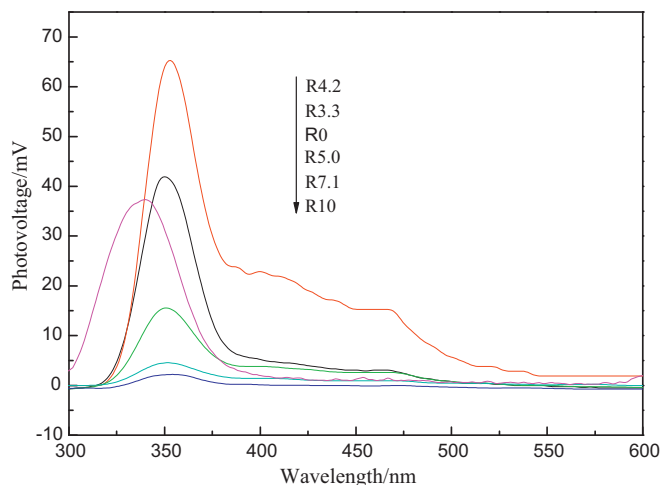


Fig. 3. SPS spectra of different TiO<sub>2</sub> photocatalysts.

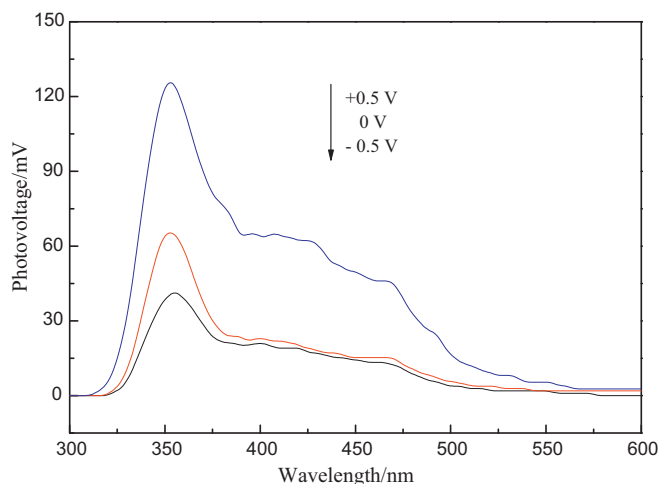


Fig. 4. Surface photovoltage spectra of R4.2 under different electrical fields.

promote the separation efficiency of photoinduced charge carriers. Interestingly, the order of the SPS response was the same as the order of the light absorption in visible region. In addition, it can be noted that the light absorption edge of cystine modified TiO<sub>2</sub> was red shifted to 570 nm, which was attributed to the following aspect. The non-metal element was doped into the lattice of TiO<sub>2</sub>, which resulted in the narrow of the band gap. As a result, the light absorption in visible region and separation efficiency of the photoinduced charge carriers were greatly improved.

Fig. 4 showed the electric field induced surface photovoltage spectra of R4.2 sample. As seen from Fig. 4, when an external electric field was employed, a remarkable change of SPS response could be observed. When a positive electric field was applied, the SPS intensity markedly enhanced, which was attributed to the same direction of added-outer and built-in field. Further, the SPS response became broad, which was ascribed to trap-to-band transitions from the surface states. On the contrary, the SPS response decreased while a negative electrical field was added, which was the common characteristic of n-type semiconductors. Thus, it can be concluded that the cystine modified TiO<sub>2</sub> in this study was still n-type semiconductor [16].

#### 4. Conclusions

Based on the above systematic analysis, several conclusions can be drawn as followed. (1) Visible light photoresponse of TiO<sub>2</sub> NPs were successfully synthesized through simple sol-gel reactions by the addition of biomolecule cystine. (2) The phase transformation of TiO<sub>2</sub> from anatase to rutile and the crystallite sizes were greatly inhibited by modification with cystine. (3) The separation efficiency of photoinduced charge carriers was significantly improved. Moreover, it can be suggested that for cystine modified TiO<sub>2</sub>, the stronger light absorption in visible region is, the higher the SPS response is.

#### Acknowledgments

The authors wish to gratefully acknowledge the financial support by National Natural Science Foundation of China for Youth (21106035) and Youth Scholar Backbone Supporting Plan Project for general colleges and universities of Heilongjiang Province (1151G034).

#### References

- [1] M.S. Hoffman, S. Martin, W. Chio, Chem. Rev. 95 (1995) 69–96.
- [2] M. Grätzel, Nature 414 (2001) 338–344.
- [3] M. Andersson, L. Osterlund, S. Ljungstrom, A. Palmqvist, J. Phys. Chem. B 106 (2002) 10674–10679.
- [4] Y. Zhu, J. Shi, Z. Zhang, C. Zhang, X. Zhang, Anal. Chem. 74 (2002) 120–124.
- [5] S.K. Joung, T. Amemiya, M. Murabayashi, K. Itoh, Chem. Eur. J. 12 (2006) 5526–5534.
- [6] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 293 (2001) 269–271.
- [7] A. Solbrand, A. Henningsson, S. Sodergren, J. Phys. Chem. B 103 (1999) 1078–1083.
- [8] S. Kohtani, A. Kudo, T. Sakata, Chem. Phys. Lett. 206 (1993) 166–170.
- [9] M. Bowker, P. Stone, R. Bennett, N. Perkins, Surf. Sci. 511 (2002) 435–448.
- [10] T. Ohno, T. Tsubota, K. Nishijima, Z. Miyamoto, Chem. Lett. 33 (2004) 750–751.
- [11] L.Q. Jing, H.G. Fu, B.Q. Wang, D.J. Wang, B.F. Xin, S.D. Li, J.Z. Sun, Appl. Catal. B 62 (2006) 282–291.
- [12] Y.Q. Wang, X.J. Yu, D.Z. Sun, J. Hazard. Mater. 144 (2007) 328–333.
- [13] J. Wang, L.Q. Jing, L.P. Xue, Y.C. Qu, H.G. Fu, J. Hazard. Mater. 160 (2008) 208–212.
- [14] Q.H. Zhang, L. Gao, J.K. Guo, Appl. Catal. B: Environ. 26 (2000) 207–215.
- [15] L.Q. Jing, Z.L. Xu, J. Shang, X.J. Sun, W.M. Cai, H.G. Fu, Sol. Energy Mater. Sol. Cells 79 (2003) 133–151.
- [16] Y.A. Cao, L. Ding, Y. Ma, Z.S. Guan, T.F. Xie, X.T. Zhang, Z.Y. Wu, Y.B. Bai, T.J. Li, J.N. Yao, Y. Wu, Chem. J. Chin. Univ. 20 (1999) 1787–1789.