

14. Barthel, J., Gores, H. -J., Neueder, R. and Schmid, A., *Pure Appl. Chem.*, **71**, 1715 (1999).
15. Côté, J. -F., Perron, G., Desnoyers, J.E., Benson, G. C. and Lu, B. C. -Y, *J. Solution Chem.*, **27**, 685 (1998).
16. Côté, J. -F., Perron, G. and Desnoyers, J.E., *J. Solution Chem.*, **28**, 395 (1999).
17. Reichstädter, L., Fischchervá, E. and Frischer, O., *J. Chem. Solution*, **1**, 35 (1999).
18. Handbook of Chemistry and Physics, 82<sup>nd</sup> ed., C. R. C. press, London, (2001)
19. Jansen, M. and Yeager, H. L., *J. Phys. Chem.*, **77**, 3089 (1973)
20. Salomon, M. and Plichta, E. J., *Electrochem. Acta*, **30**, 113 (1985)
21. Kita, F.A., Snoda, T. and Kobayashi, H. "In new sealed Rechargeable batterie and supercapacitors", B. M.Barnet, E. Dowgiallo, G. Halper, Y. Matsuda, and Z-i Takehara, Editors, PV93-23, P.321, The Electrochemical Society Proceeding series, Pennington, NJ (1993)
22. Hasegawa, K. and Arakawa, Y., *J. Power Sources*, **44**, 523 (1993).
23. Debye, P. and Hückel, E., *Phys. Z.* **24**, 185(1923).
24. Jackson, M. D. and Gilkerson, W. R., *J. Am. Chem. Soc.*, **101**, 328 (1979).
25. Gilkerson, W. R. and Kendrick, K. L., *J. Phys. Chem.*, **88**, 5352 (1984)

Submitted 12<sup>th</sup> July 2001  
Revised 18<sup>th</sup> October 2001

## THE SENSITIZATION OF SELF-ASSEMBLED MONOLAYER FORMED BY OCTADECANETHIOL FOR THE PHOTO-ELECTRIC OXIDATION OF CH<sub>3</sub>OH ON THE TiO<sub>2</sub> NANOPOROUS FILM ELECTRODE

Keqiang Ding <sup>a,b\*</sup>, Zhenbin Jia <sup>a</sup>, Jianglin Cao <sup>a</sup>, Ruting Tong <sup>a</sup>, Xinkui Wang <sup>b</sup>

<sup>a</sup> Department of Chemistry, Hebei Normal University, Shijiazhuang 050016, P.R. China.  
E-mail: dkeqiang@263.net

<sup>b</sup> Institute of Coal Chemistry, Chinese Academy of Science, Taiyuan 030001, P.R. China

### Abstract

Octadecanethiol self-assembled monolayer (OCSAM), which was first employed as one sensitizer for TiO<sub>2</sub> nanoporous film electrode in the oxidation of methanol, was firstly investigated using electrochemical and photoelectrochemical methods. The photocurrent generated by using TiO<sub>2</sub> nanoporous film electrode modified by OCSAM (18SH/TiO<sub>2</sub>) is about 1.95 times larger than that without modification. In addition, the maximum absorption peak has shifted towards the infrared region for about 30nm when the TiO<sub>2</sub> nanoporous film electrode modified with OCSAM. This paper has testified that the increased photocurrent could not be attributed to the photooxidization of octadecanethiol or the ethanol solvent simply. It was proposed that the change of surface structure of TiO<sub>2</sub> nanoporous film electrode should be responsible for the phenomenon in some degree.

**Keywords:** Octadecanethiol; Self-assembled monolayer; Sensitization; TiO<sub>2</sub> nanoporous film electrode; Photoelectrooxidation

### Introduction

So far there are many papers dealing with TiO<sub>2</sub> electrode or TiO<sub>2</sub> nanoporous film electrode with an intention to improve the light-to-electricity conversion efficiency. The dye-sensitized photoelectrochemical cells have been widely investigated because of their characteristics of differentiating light absorption and charge separation. Many organic substance was tried to improve the conversion efficiency[1-4]. Some noble metals, such as platinum and ruthenium, were also employed to sensitize the TiO<sub>2</sub> electrode[ 5,6]. Summarily, dye, nanoporous film, and noble metal are the three main sensitizers for TiO<sub>2</sub> electrode. Nanoporous sulfide was also used to sensitize the TiO<sub>2</sub> nanoporous films electrode and TiO<sub>2</sub> self-assembled monolayer electrode[7, 8], where the light absorption of TiO<sub>2</sub> photoanodes could be extended into the visible region. In a word, the investigation of improving the conversion efficiency of light to electricity for TiO<sub>2</sub> has never been terminated.

Alkyl thiol self-assembled monolayer (SAM), due to its specific character, has been widely applied in the areas, such as mimicking biomembrane, molecular distinction, corrosion protection, electrocatalysis [9, 10]. Its photochemical behavior has also been reported, but mostly the self-assembled monolayer was attached to Au or Ag substrate [11, 12].

Photoelectrooxidation of methanol on TiO<sub>2</sub> nanoporous film electrode has been reported [13, 14], and it revealed that the adsorption of -OH group on the surface of TiO<sub>2</sub> was the first step in the process of photoelectrooxidation of methanol [15]. The similar chemical nature between -OH and -SH group motivates us to try the formation of SAM by alkanethiol on the surface of TiO<sub>2</sub> nanoporous electrode. Theoretically, it was believed that the diameter of TiO<sub>2</sub> particle is about 10 times longer than the thickness of self-assembled monolayer of octadecanethiol [16]. So that it is reasonable to believe that self-assembled monolayer could form on the surface of TiO<sub>2</sub> partly.

Still now, there is no paper considering TiO<sub>2</sub> nanoporous film electrode modified with the SAM of alkylthiol in methanol fuel solar cell. This paper not only proved the formation of SAM on TiO<sub>2</sub> nanoporous film electrode with the cyclic voltammetry (CV) technique but also verified the sensitization of SAM for the TiO<sub>2</sub> nanoporous film electrode in the oxidation of methanol directly. The results demonstrated that the photocurrent was improved by about 95% when the TiO<sub>2</sub> nanoporous electrode was modified with self-assembled monolayer. The shifting phenomenon of maximum absorption peak to the infrared region was observed clearly. Both the possible mechanism and further application of this sensitizer have been discussed.

### Experimental

The advantages of TiO<sub>2</sub> nanoporous film electrode have been confirmed by recent literature [17]. TiO<sub>2</sub> nanoporous film electrode was fabricated according to the process shown before [18]. A piece of 2cm×3cm conducting glass was dipped into the mixture solution containing TiO<sub>2</sub> nanoporous particles and carbonwax reagent. The immersed time was 2s, and then picking the conducting glass up, after the solution has rolled down, immersing it in the solution once again. The process was repeated 3 times for each conducting glass. And then, after being blew dry, it was sintered at 420 °C for 30 min in an ambient atmosphere. The exposed area of the transparent TiO<sub>2</sub> nanoporous film electrode was 0.5cm<sup>2</sup>, where the edge was sealed with epoxy resin. The scanning electron micrograph proved these particles to be in the range from 20nm to 30nm.

Prior to self-assembly process, TiO<sub>2</sub> nanoporous film electrode was rinsed with water and blown dry with high pure nitrogen. The treated TiO<sub>2</sub> nanoporous electrode was introduced into the anhydrous ethanol solution containing 0.1mM octadecanethiol. After 24 hour, it was assumed that the forming of octadecanethiol modified electrode (18SH/TiO<sub>2</sub>) has been accomplished. Before using it, both ethanol and distilled water were all utilized to wash it successively.

The conventional three-electrode cell was used in the electrochemical measurements. A large Pt foil and one Saturated Calomel Electrode (SCE) were used as the counter and reference electrode, respectively. One Princeton Applied Research (PAR) model 273 potentiostat was involved. Photocurrent measurement was carried out with the above instruments too, besides, one isom Xenon lamp (150W) was used to create illumination. A monochromator placed in the path of illumination was used to create monochromatic light. 0.1M Na<sub>2</sub>SO<sub>4</sub> solution containing 0.04M methanol was employed as the electrolyte to measure the photocurrent as well as the current. All other reagents were analytical grade. The solvent used here was the distilled water.

### Results and Discussion

The sensitization of the self-assembled monolayer formed octadecanethiol for the oxidation of methanol has been illustrated in figure.1 clearly. The cyclic voltammograms for TiO<sub>2</sub> nanoporous film electrode was presented by line c, which was recorded in methanol solution after 1 min's illumination. The photocurrent was measured to be about 0.14mA. But for the 18SH/TiO<sub>2</sub> electrode, as was shown by line b, the photocurrent has been increased by about 95% compared to TiO<sub>2</sub> electrode. The magnificent augment of the photocurrent excited us to pursuit the reason. In order to probe the influence of illumination, the illumination time was prolonged to 1h and then the CV plots were recorded. Unexpectedly, the photocurrent was increased from 0.27mA to 0.29mA, No attenuation was observed. As usual, it is very easy for us to assume that the photoelectrooxidation of 18SH or ethanol solvent will lead to the increased photocurrent at first and then the photocurrent should drop to its former value or at least should become some smaller. Namely, if the film has been oxidized, the photocurrent should have diminished to 0.14mA or to some smaller value. But the result is opposite to our supposing. The phenomenon strongly supported that the SAM of octadecanethiol on TiO<sub>2</sub> has not been destroyed by 1h's illumination, which agrees with the previous literature very well [19].

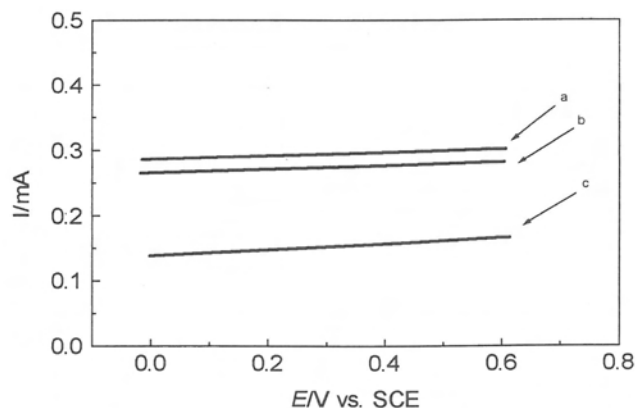


Figure 1. The cyclic voltammograms of different electrodes under the same illumination condition in 0.04M methanol solution containing 0.1M Na<sub>2</sub>SO<sub>4</sub>, scan rate 100mV/s; a: 18SH/TiO<sub>2</sub> after the illumination for 1h b: 18SH/TiO<sub>2</sub> after the illumination for 1 min; c: TiO<sub>2</sub> nanoporous film electrode.

To distinguish the effect of octadecanethiol from that of C<sub>2</sub>H<sub>5</sub>OH on the increased photocurrent, we generated ethanol-modified TiO<sub>2</sub> electrode using the same process. As a result, the photocurrent was increased by about 10% through using the ethanol-modified TiO<sub>2</sub> electrode, suggesting that the existence of ethanol on the surface of TiO<sub>2</sub> had done a little contribution to the improved photocurrent, which was shown in figure 2. The results enabled us to draw the following conclusion that the increased photocurrent was mainly caused by SAM of octadecanethiol, i.e., octadecanethiol's SAM has sensitization for TiO<sub>2</sub> nanoporous film electrode in the photoelectrooxidation of methanol.

To determine the formation of self-assembled monolayer by octadecanethiol, the CV technique was also applied to the above system, which was carried out without illumination. The results have been displayed in figure 3. Obviously, for TiO<sub>2</sub> electrode, there is an oxidative peak appearing at 0.42V, where the oxidative peak could only be attributed to the oxidation of methanol in the studied solution.

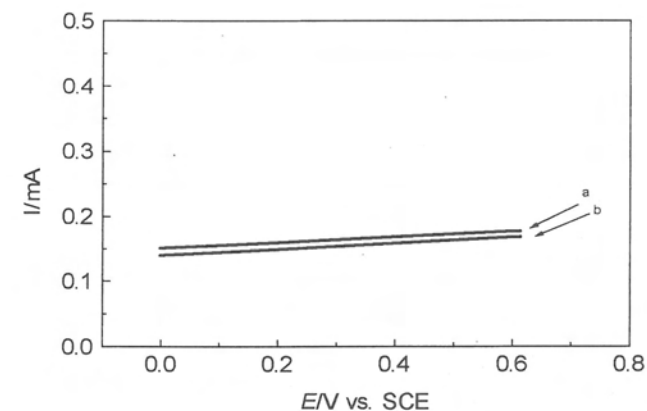


Figure 2. The comparison of cyclic voltammograms between two electrodes under illumination for 1min in 0.04M methanol solution containing 0.1M Na<sub>2</sub>SO<sub>4</sub>, scan rate 100mV/s; a: TiO<sub>2</sub> nanoporous film electrode modified with ethanol; b: TiO<sub>2</sub> nanoporous film electrode.

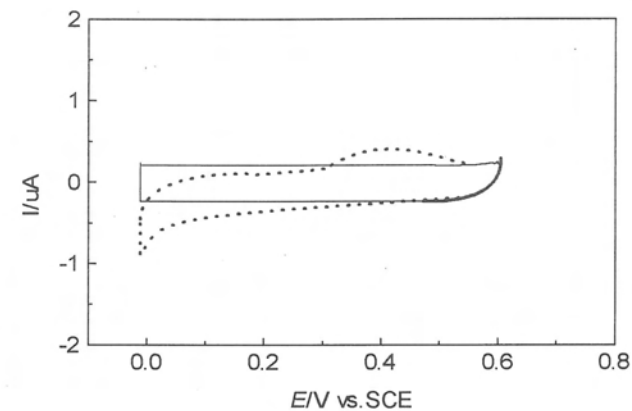


Figure 3. The cyclic voltammograms of different electrodes without illumination in 0.04M methanol solution containing 0.1M Na<sub>2</sub>SO<sub>4</sub>, scan rate 100mV/s methanol solution; (.....): TiO<sub>2</sub> electrode; (—): 18SH/TiO<sub>2</sub> electrode.

Whereas, for the 18SH/TiO<sub>2</sub> electrode, the oxidative peak did not appear, in which there is only one rectangle graph instead, which accords with the formation of self-assembled monolayer[19]. The difference between the CV plot of TiO<sub>2</sub> and that of 18SH/TiO<sub>2</sub> electrode strongly confirmed the formation of SAM. So we could think that the improved photocurrent only be generated by the SAM of octadecanethiol.

We also studied the influence of wavelength on the photocurrent for the 18SH/TiO<sub>2</sub> and TiO<sub>2</sub> electrode, which were carried out under the same illumination intensity and polarization potential (0.3V vs SCE). The plot we recorded was called IPCE spectrum, which was shown in figure.4. It is evident that at the maximum adsorption peak (MAP), the photocurrent for the 18SH/TiO<sub>2</sub> electrode is 1.54 times larger than that for the single TiO<sub>2</sub> nanoporous film electrode. What's more, the MAP has extended to the infrared region for about 30nm. The shifting phenomenon implied that due to the adsorption of octadecanethiol, the character of the surface of TiO<sub>2</sub> has altered in some degree.

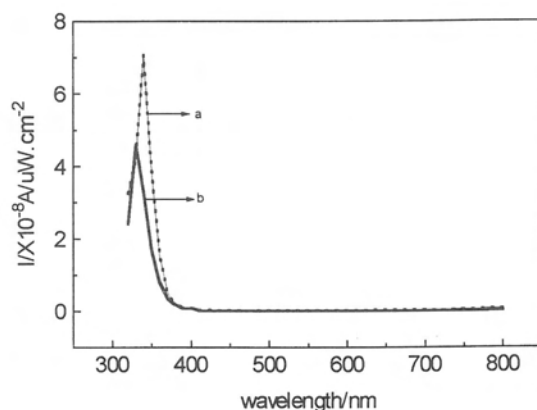


Figure 4. The photocurrent for different electrodes under the illumination condition in 0.04M methanol solution containing 0.1M Na<sub>2</sub>SO<sub>4</sub> with the varying wavelength; a: 18SH/TiO<sub>2</sub> electrode; b: TiO<sub>2</sub> electrode.

Though the formation of SAM by octadecanethiol has been confirmed by the CV, we still think that the densely packed SAM could not form due to the uneven surface of TiO<sub>2</sub>. So we transferred the 18SH/TiO<sub>2</sub> electrode into 1mM K<sub>3</sub>Fe(CN)<sub>6</sub>/K<sub>4</sub>Fe(CN)<sub>6</sub> solution to investigate the character of SAM(not shown). As a result, there is one pair of nearly reversible peaks appearing, which notes that the formed SAM is loose enough for the inorganic ions to reach the TiO<sub>2</sub> surface easily. Hence, combining above results, we proposed that "microscopic ordered region" has come into being on the surface of TiO<sub>2</sub> electrode. The formation of "microscopic ordered region" could influence the diffusion process of methanol, while for the inorganic ions, the loose structure could not prevent it from diffusing. So we suggested that the different diffusing behavior between methanol and inorganic ion should be responsible for the varied cyclic voltammograms.

#### Final Comments

What we have obtained surely encouraged us to seek the reason that made the photocurrent increased. We thought that there were two ways to bring out both the improved photocurrent and the shifting phenomenon to infrared region. Firstly, the polarity of TiO<sub>2</sub> surface will diminish owing to the adsorbed octadecanethiol, which will validate the access of CH<sub>3</sub>OH to the surface of TiO<sub>2</sub>. The second one is probably due to "microscopic ordered region", which was created by self-assembled monolayer of octadecanethiol, i.e., the structure of the "double electric layer" of TiO<sub>2</sub> has been changed.

In a word, the experiments we have carried out above have indicated that the sensitization of self-assembled formed by octadecanethiol for TiO<sub>2</sub> to oxidize CH<sub>3</sub>OH under illumination was significant. Our work in this paper offered the increased photocurrent and the infrared shifted phenomenon as well. Further experiments we performed have proved that the increased photocurrent could not be attributed to the oxidation of octadecanethiol or ethanol simply. After analyzing the above results, we proposed that the formation of "microcosmic ordered region" on the surface of TiO<sub>2</sub> has changed the character of the surface or the double electric layer of TiO<sub>2</sub> electrode, which probably has affected the reaction mechanism between photon and electron donors.

The main contribution of this work is to develop one new application of self-assembled monolayer, which probably has provided a model to reveal the catalytic

mechanism of organic molecules for TiO<sub>2</sub> electrode. All other detailed studies are being carried out.

#### References

1. F.R.F. Fan, A.J. Bard, *J. Am. Chem. Soc.*, 101 (1979) 6139.
2. V.H. Houlding, M. Gratzel, *J. Am. Chem. Soc.*, 105 (1983) 5695.
3. J. Moser, M. Gratzel, *J. Am. Chem. Soc.*, 106 (1984) 6557.
4. M.K. Nazeeruddin, A. Kay, I. Rodicio, *J. Am. Chem. Soc.*, 115 (1993) 6382.
5. J. Sotomayor, R.W. Hoyle, G. Will, D. Fitzmaurice, *J. Mater. Chem.*, 8 (1998) 105.
6. W. Choi, A. Termin, M. R. Hoffmann, *J. Phys. Chem.*, 98 (1994) 13669.
7. R. Vogel, P. Hoyer, H. Weller, *J. Phys. Chem.*, 98 (1994) 3183.
8. C. Miller, P. Cuendet, M. Gratzel, *J. Phys. Chem.*, 95 (1991) 877.
9. J. Cheng, S. S. Gotthard, A.T. John, J.M. Cary, *J. Am. Chem. Soc.*, 118 (1996) 680.
10. O.W. Michael, A. F. Marye, *J. Am. Chem. Soc.*, 117 (1995) 1845.
11. D.L. Jiang, J.X. Li, P. Diao, *J. Photochem. Photobiol. A: Chemistry*, 132 (2000) 219.
12. H. Gerisher, A. Heller, *J. Phys. Chem. B.*, 95 (1991) 5261.
13. P.A. Mandelbaum, A.E. Regazzoni, M.A. Blosa, S.A. Bilmes, *J. Phys. Chem.*, 103 (1999) 5505.
14. H. K. Yang, H. Xue, T.H. Lu, *J. Chem. Chin. Univ.*, 19 (1998) 1320.
15. J.M. Kesselman, O. Weres, N.S. Lewis, M.R. Hoffmann, *J. Phys. Chem. B*:101 (1997) 2637.
16. K. Slowinski, R.V. Chamberlain, C.J. Miller, M. Majda *J. Am. Chem. Soc.*, 119 (1997) 11910.
17. Y.Z. Hao, M. Yang, C. Yu, S. M. Cai, *Solar. Energy. Mater. Sol. Cells.*, 56 (1998) 75.
18. L.F. Rozsnyai, M.S. Wrighton, *J. Am. Chem. Soc.*, 116 (1994) 5993.
19. P. Diao, D.L. Jiang, X.L. Cui, *J. Electroanal. Chem.*, 464 (1999) 61.

Submitted 26<sup>th</sup> October 2001  
Accepted 11<sup>th</sup> January 2002

## ELECTROCHEMICAL SURFACE MODIFICATION OF ALUMINUM-SURFACE PROFILING BY INTERFEROMETRY

M. Anbu Kulandainathan,\* R. Diaz and F. Sanz  
Dept of Physical Chemistry, University of Barcelona,  
Av. Diagonal 647, 08028-Barcelona, SPAIN

Preliminary  
Communication

**Abstract** – The surface analysis using interferometry studies clearly indicates that the oxidation cycling at high frequency at aluminum electrode in the 0.1M NaClO<sub>4</sub> containing 10 mM sodium tetraphenylborate solution yields selective dissolution of faces other than (111) by forming pyramidal shape voids that is not due to the simultaneous dissolution and redeposition as in the case of Pt. It is also confirmed that surface smoothing and flattening on the aluminum surface is due to flattening process and the formation of voids are due to electrochemical dissolution.

**Key words:** aluminum, interferometry, faceting, and hydrophobic additive

### INTRODUCTION

The status on reconstructed electrode surfaces has been summarised, placing emphasis on the in-situ scanning microscopy studies in a recent review by Kolb [1]. The author also describes the conditions under which reconstructed surfaces are stable in solution and describes about the potential induced reconstruction and the transition between reconstructed and unreconstructed surfaces. The modification of electrode surface has been done by employing different techniques, namely: sputter and annealing in UHV, Flame annealing and potential-induced reconstruction. The most widely used one is the repetitive oxidation/reduction cycling in a suitable electrolyte in high frequency. Due to this potential cycling, there is an increase in roughness and

\* On leave from Central Electrochemical Research Institute, Karaikudi, India.

Email: manbu123@yahoo.com