

THE SENSITIZATION OF SELF-ASSEMBLED MONOLAYER FORMED BY OCTADECANETHIOL FOR THE PHOTOELECTROOXIDATION OF CH₃OH ON TiO₂ NANOPOROUS FILM ELECTRODE

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The aim of this paper is to present the sensitization of self-assembled monolayer formed by octadecanethiol for the photoelectrooxidation of CH₃OH on TiO₂ nanoporous film electrode for the first time.

So far there are many papers dealing with TiO₂ electrode or TiO₂ nanoporous film electrode with an intention to improve the light-to-electricity conversion efficiency^{1,2}. Meanwhile, since its inception, the self-assembled monolayer (SAM) has been widely applied in some particular areas^{3,4}. Its photochemical behavior has also been reported, but generally the self-assembled monolayer was attached to Au or Ag substrate^{5, 6}. Recently, due to its potential application in the solar cell, the photoelectrooxidation of CH₃OH has also attracted much more attention.

To the best of our knowledge, there is no paper reporting the sensitization of self-assembled monolayer for the photoelectrooxidation of CH₃OH, especially on TiO₂ electrode.

TiO₂ nanoporous film electrode was prepared on the basis of former literature. Prior to the formation of self-assembled monolayer, TiO₂ nanoporous film electrode was rinsed with water and blown dry with high pure nitrogen. And then the treated TiO₂ nanoporous electrode was transferred into the anhydrous ethanol solution containing 0.1mM octadecanethiol for 24 h. After being blown dry, the electrode was dipped in 0.1M Na₂SO₄ solution containing 0.04M methanol, which was employed as the measuring system.

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. A Princeton Applied Research (PARC) model 273 potentiostat was used to measure the photocurrent as well as current, besides, one isom Xenon lamp (150W) was used to create light. A monochromator placed in the path of illumination was used to create monochromatic light. All other reagents were analytical grade.

The remarkable sensitization of the self-assembled monolayer formed by octadecanethiol for the photoelectrooxidation of methanol has been illustrated in Figure.1 clearly. The cyclic voltammogram for TiO₂ nanoporous film electrode is represented by line c, which was recorded in methanol solution after 1 min's illumination. And its photocurrent was measured to be about 0.14mA. But for the TiO₂ nanoporous film electrode modified with octadecanethiol (18SH/TiO₂), the photocurrent was increased by about 95% compared to TiO₂ electrode unexpectedly, which was shown by the comparison between line b and line c. The magnificent augment of the photocurrent really excited us. In order to probe the influence of illumination, the illumination time was prolonged to 1h and then the cyclic voltammogram was recorded. Interestingly, the photocurrent was increased from 0.27mA to 0.29mA, and no attenuation was observed. As usual, it is very easy for us to think that the photoelectrooxidation of 18SH will lead to the increased photocurrent at first and then the photocurrent should drop to its original value or at least should become somewhat 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 indicates that the sensitization of SAM of octadecanethiol for the photoelectrooxidation of methanol on TiO₂ is not only significant, but also the SAM could not be destroyed by 1h's illumination, which is meaningful to explore the self-assembled monolayer's new application.

As we know, many organic substances could sensitize the photocurrent occurring on TiO₂ electrode, but their catalytic mechanisms have not been revealed very well. Here the phenomenon we observed is useful to reveal the organic substance catalytic mechanisms in molecular level.

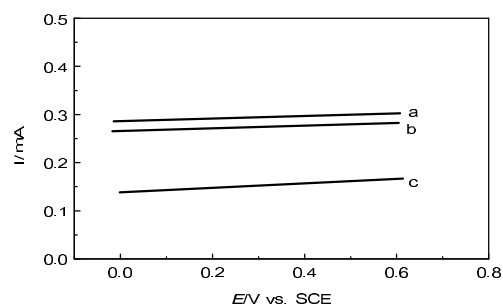


Figure1. The cyclic voltammograms of different electrodes under the same illumination condition in methanol solution: (a) 18SH/TiO₂ electrode after the illumination for 1h; (b): 18SH/TiO₂ after the illumination for 1 min, (c): TiO₂ nanoporous film electrode.

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