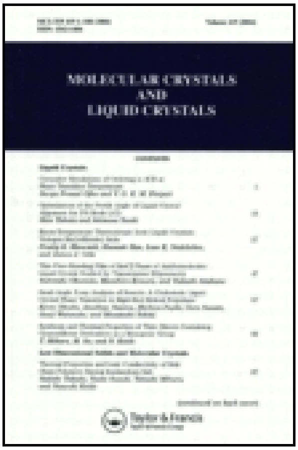

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Electrochemical and Photoelectrochemical Properties of ITO/α-Fe_2O_3 Nanoparticulate Film Electrode in Na_2SO_4 Solution

Xinming Qian [a], Xingtong Zhang [c], Xin Ai [a], Yanzhong Hao [b], Fengqi Liu [a], Shengmin Cai [b], Yubai Bai [a], Tiejin Li [a], Xinyi Tang [a] & Jiannian Yao [c]

[a] Department of Chemistry, Jilin University, Changchun, 130023, P. R. China

[b] College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, P. R. China

[c] Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing, 100101, P.R. China

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Electrochemical and Photoelectrochemical Properties of ITO/α-Fe_2O_3 Nanoparticulate Film Electrode in Na_2SO_4 Solution

XINMING QIAN[a], XINGTONG ZHANG[c], XIN AI[a],
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TIEJIN LI[a], XINYI TANG[a] and JIANNIAN YAO[c]

[a]*Department of Chemistry, Jilin University, Changchun 130023, P. R. China,* [b]*College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China and* [c]*Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing 100101, P.R.China*

The electrochemical and photoelectrochemical properties of ITO/α-Fe_2O_3 nanoparticulate film electrode were investigated using voltammetry and optically induced photocurrent transient measurements. The mechanism of photoinduced electron-hole(e-h) transported within the semiconductor film was discussed in detail.

Keywords: Electrochemistry and photoelectrochemistry(EC-PEC); α-Fe_2O_3; nano-particulate film

INTRODUCTION

In recent years, semiconductor particulate films have received much attention for applications in photocatalytic devices, dye-sensitized solar cells. These semiconductor films with high porosity could improve the light-to-electrical-energy-conversion efficiency of the electrode in the photoelectrochemical cells(PEC)[1]. The investigations of nanocrystalline semiconductor films in PEC have shown that no space-charge layer is formed in the nanoporous films and that the charge-separation process is controlled by the different rates of electrons or holes transfer to the electrolyte at the semi-conductor electrolyte interface[2]. In this paper, α-Fe_2O_3 nanoparticulate films were fabricated on ITO electrode by coating technique. The EC-PEC properties of this electrode were studied in Na_2SO_4 solution.

EXPERIMENTAL SECTION

The α-Fe_2O_3 colloid was synthesized by a forced hydrolysis method reported previously[3]. The diameter of these particles was around 45nm which was determined by TEM technique (TEM 2000-FX). The UV-vis spectrum was obtained using a Shimadzu 3100UV-vis-near-IR spectrophotometer.

ITO/α-Fe_2O_3 electrodes were prepared following a procedure described elsewhere[4]. EC-PEC experiments were carried out in a cell with a quartz window, consisting of Pt counter electrode and SCE reference electrode in 1M Na_2SO_4 solution. The voltammetry experiments were performed with PAR M173 potentiostat, driven by a Model 175 universal programmer. The photocurrent-time profile experiment was carried out with a PAR M 5206 lock-in amplifier. As a light source, a 200W Xenon lamp was used.

RESULTS AND DISCUSSION

Fig.1 shows the optical absorption spectrum of α-Fe_2O_3 colloid. From the absorption spectrum, the onset of absorption starts below 560nm, which is in excellent agreement with the reported band-gap energy for α-Fe_2O_3 of 2.2eV. Fig. 2 shows the linear scan voltammogram of ITO/α-Fe_2O_3 film electrode in 1M Na_2SO_4 solution in the dark and under illumination. In the dark, very large cathodic current is seen as a result of accumulation of electrons in the vacant electron states of α-Fe_2O_3 film. Under illumination, in the anodic region, the photocurrent gradually increases along with an increase of the anodic applied voltage. The generation of anodic photocurrent is a characteristics behavior of n-type semiconductor as is well known. Moreover, the linear voltammetry characteristics also gives a qualitative estimate of the flatband potential of the semiconductor. The flat-band potential (E_{fb}) of α-Fe_2O_3 film is assumed to be approximately the same as the photocurrent onset potential[5]. From Fig.2, the E_{fb} of α-Fe_2O_3 film in 1M Na_2SO_4 solution is at +0.1V vs. SCE..

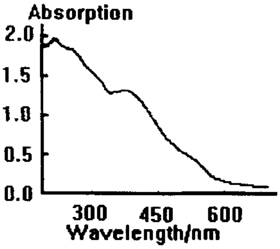

FIGURE 1. UV-vis absorption spectrum of α-Fe_2O_3 colloid.

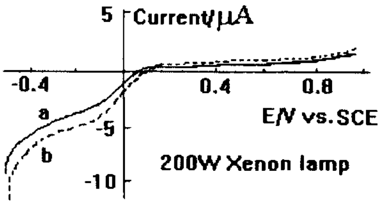

FIGURE 2. Linear scan voltammogram of ITO/α-Fe_2O_3 electrode in Na_2SO_4 solution

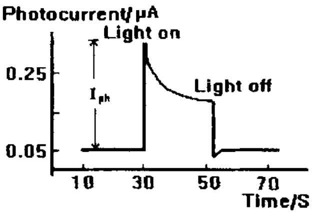

FIGURE 3. Photocurrent-time profile of ITO/α-Fe_2O_3 electrode in Na_2SO_4 solution. Bias: +0.4V vs.SCE

Fig.3 shows the photocurrent-time characteristics of ITO/α-Fe_2O_3 electrode in 1M Na_2SO_4 solution at a constant potential of 0.4V (vs.SEC). Upon illumination, the anodic photocurrent was prompt and was followed by a rapid decay. The rapidly increased photoanodic current suggests the photo-generated holes move to α-Fe_2O_3 film surface where they are scavenged by OH^- in the solution, while the photo-electrons flow toward the ITO back-electrode. The dacay of I_{ph} is mostly due to the fact that the photogenerated electrons and holes are more prone to recombination. Further, the decrease of OH^- in the local concentration may contribute to the decay in I_{ph} with time. When the illumination is cut off, a cathodic current is observed in α-Fe_2O_3 film electrode. This reversal of current indicates that the electrons flow toward the electrolyte to reduce the electron acceptor O_2 presented in the solution at the α-Fe_2O_3/electrolyte interface and the product of the oxidation of OH^- with holes within the pores of α-Fe_2O_3 film. Such a flow of electrons in both directions in α-Fe_2O_3 thin films indicates no space-charge layer can be formed at the α-Fe_2O_3/electrolyte interface. So, the charge separation occurs at α-Fe_2O_3/electrolyte interface not by a space-charge layer, but rather by differing rate of electrons and holes transfering into solution.

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