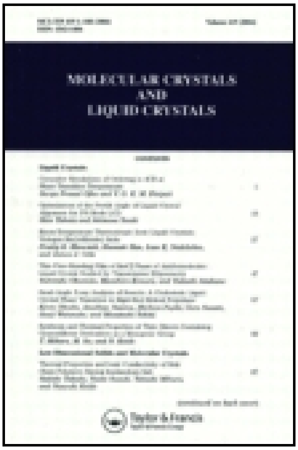

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Zirconium Phosphonate Multilayers of Organic Redox Couples on Nanocrystalline TiO_2 Semiconductor Electrode

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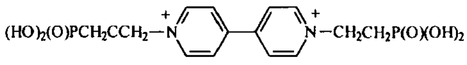
New type of surface modification of redox-couple multilayers on nanoporous TiO_2 film has been demonstrated. N,N'-bis(ethylphosphonic acid)-4,4'-bipyridinium chloride(VP) and N,N'-bis(ethyl dihydrogen phosphate)-3,4,9,10-perylene bis(dicarboximide)(EPPI) were directly coordinated at surface defect site Ti^{4+} of nanoporous TiO_2 film electrode. The sequential adsorption by alternating treatment of $ZrOCl_2$ and VP or EPPI allows building up zirconium phosphonate multilayers of the redox couples. Cyclic voltammetry and UV-visible absorption measurement have shown the systematic layer-by-layer growing of the multilayers and the heterogeneous electron-transfer from TiO_2 conduction band to the redox couples multilayers. The estimated average amount of the redox couples in each layer on the electrode was about 1.0×10^{-11} mole/cm^2 which is in agreement with the reported density of states assigned to surface Ti^{4+} sites.

Keywords: metal phosphonate multilayer; nanocrystalline TiO_2; viologen derivative; perylenebis(dicarboximide) derivative

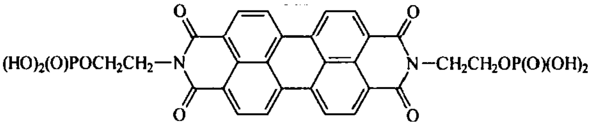
INTRODUCTION

Langmuir-Blodgett technique has been known for a long time to be an excellant method for preparing mono- or multilayer organic thin films and a lot of interesting molecular systems assembled in this technique have been demonstrated and studied.[1] However, this technique suffers several drawbacks such as a high sensitivity to contaminants, low thermal stability, large number of mechanical manipulation and requirement of planar substrate etc. Metal phosphonate multilayer technique initiated by Mallouk and coworkers[2] has been paid great attention in preparing controllable multilayer structure. The method is based on the sequential adsorption of metal ion and bisphosphonic acid. The films, prepared by this technique, are highly stable to the thermal, mechanical and chemical stress and do not require a planar substrate. It can be grown even on high-surface silica gel.[3]

Here we report the preparation of reversible electron-acceptor multilayers, which are viologen diethylphosphonic acid (VP) and perylenebis(dicarboximide) derivatives (EPPI), on the nanoporous semiconductor electrode using the metal phosphonate multilayer technique and electrochemical and spectroelectrochemical studies of electron transfer from semiconductor electrode to the electron-acceptor multilayers.



VP



EPPI

EXPERIMENTAL

The electrochemical measurement was carried out in an argon-purged one-compartment cell, equipped with a platinum counter electrode and SCE reference electrode. The cyclic voltammetry was measured using an EG & G PAR 263A potentiostat. Spectroelectrochemical measurements were performed with a conjuction of Hitachi U-3210 spectrophotometer and PAR 263A potentiostat. The morphologies and film thicknesses of nanoporous semiconductor films were determined using Hitachi S-2700 scanning electron microscope. Deionized water was purified to a resistivity of 18 MΩcm by Barnstead Nanopure II water purification system.

Synthesis of VP and EPPI

N, N'-bis(ethylphosphonic acid)-bipyridinium chloride (VP) were synthesized similarly as reported elsewhere[4]. 4,4'-bipyridine and diethyl 2-bromoethyl phosphonate were refluxed in acetonitrile. The resulting ester was hydrolyzed with concentrated HCl solution to give the phosphonic acid chloride salt. N,N'-bis(ethyl dihydrogen phosphate)-3,4,9,10-perylene (dicarboximide) (EPPI) was prepared from the condensation reaction of 3,4,9,10-perylenedicarboxylic dianhydride and 2-

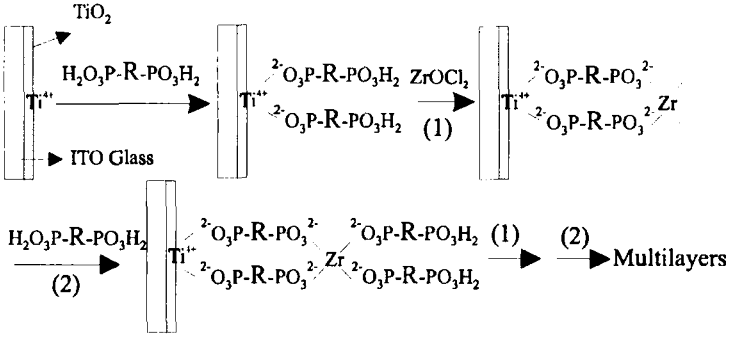
aminoethyl dihydrogen phosphate in a molten imidazole at ca. 170 °C for 2-3 hours.[5]

Preparation of Nanocrystalline Semiconductor Film Electrodes

Nanocrystalline TiO_2 film electrode was prepared following the methods of Grätzel et al.[6] 3.0 g of Degussa P25 TiO_2 powder was ground in a mortar with 1.0 ml water and 0.1 ml acetylacetone. After the powder was well dispersed, 4 ml of water and 0.05 ml of Triton X-100 was slowly added to give a TiO_2 colloidal sol. This sol was dropped on the Indium-Tin-Oxide(ITO, 40 Ω/cm^2, Delta Tech.) substrate and spread with glass rod by sliding over the tape-covered edges of ITO. After being dried in air the film was sintered at 450 °C for 2 hours. The thickness of TiO_2 film on ITO was about 4 μm estimating from scanning electron microscope picture.

Preparation of Zr-VP/Zr-EPPI multilayers on Nanoporous TiO_2 Electrode

The TiO_2 film electrode was immersed in 5 mM solution of VP at 60 °C for about 8 hours for Zr-VP film and in 1 mM EPPI solution at room temperature for 2 hours for Zr-EPPI film. After washing the electrode thoroughly with a copious amount of deionized water, it was dipped in a 10 mM $ZrOCl_2$ solution for 2 hours at room temperature same in both cases. As shown Scheme 1 the electrode was treated alternately in the solution of VP or EPPI and zirconyl chloride to build up their multilayers with thorough washing between dippings.



SCHEME 1. Sequential adsorption scheme for constructing the multilayers of Zr-VP and Zr-EPPI on the TiO_2 surface (R = VP or EPPI).

RESULTS AND DISCUSSION

Phosphonic acid-functionalized viologen(VP) and perylenebis(dicarboximide) (EPPI) compounds are directly adsorbed on the nanoporous TiO_2 film without any ancoring agent. Cyclic voltammograms of VP and EPPI layers on nanoporous TiO_2 electrode are shown in Figure 1. The background current of bare TiO_2 film electrode is associated with the charging/discharging of the accumulation layer which is equivalent to the redox process of surface defect sites Ti^{4+} of TiO_2 film.[7, 8] After adsorption of VP and EPPI on the TiO_2 film the reduction peaks of VP and EPPI are clearly seen and quasi-reversible as shown in Fig. 1. The measured formal potentials of VP and EPPI are -0.60 V and -0.55 V vs SCE, respectively.

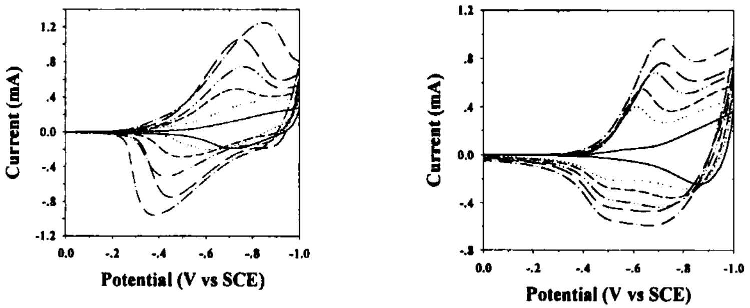


FIGURE 1. Cyclic voltammograms of Zr-VP(left) and Zr-EPPI(right) layers on nanocrystalline TiO_2 electrode(from bare TiO_2 to 5 layer-coated TiO_2 as increasing order, scan rate 25 mV/sec).

The quasi-reversible peaks are systematically increased as the numbers of layer increase in both cases. Control experiments showed that redox peaks do not increase without treatment of zirconyl chloride solution in each layer-growing step. In order to estimate the adsorbate concentration in each layer the charges which are used to reduce the Zr-VP and Zr-EPPI are calculated by integrating the cathodic peaks in the cyclic voltammograms in Fig. 1. As the layers grow, the charges are linearly increased in both cases(not shown here). It means that the adsorbate concentration in each layer is pretty constant. Considering the measured surface area of the TiO_2 film from BET experiment as 40.2 m^2/g[8] we have estimated the adsorbate concentration of 1.1×10^{-11} and 8.0×10^{-12} mole/cm^2 for Zr-VP and Zr-EPPI, respectively in each layer. These values are in the order of the known density of states of surface Ti^{4+}. Fitzmaurice et al recently showed that salicylic acid-functionalized viologen compound can be adsorbed on polycrystalline TiO_2 film and the heterogeneous electron transfer from the semiconductor to the compound can be occurred.[9] They estimated the adsorbate concentration on the TiO_2 film as about $5x10^{-11}$ mole/cm^2 and concluded that the salicylic acid in the compound is coordinated to the surface Ti^{4+} sites. Their result is well consistent with ours. Therefore one phosphonate end of VP and EPPI in the first layer is presumably coordinated at the surface Ti^{4+} sites and the next layer is linked by the coordination of Zr^{4+} ion as shown in Scheme I.

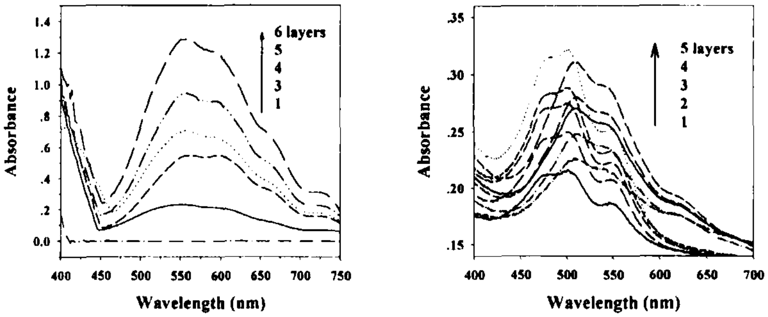


FIGURE 2. Visible absorption spectra of Zr-VP(left) and Zr-EPPI(right) films on nanoporous TiO_2 film electrode at the applied potentials, 0.0 V and 0.8 V vs SCE

The reductions of VP and EPPI compounds in these multilayers were also monitored by the spectroelectrochemical method. Figure 2 shows the visible absorption spectra of Zr-VP and Zr-EPPI multilayers on the TiO_2 film electrode at 0.0 V and -0.8 V vs SCE. Unreduced Zr-VP layers do not absorb visible light (the bottom line in Figure 2, left). The broad absorption band between 450 and 700 nm in the figure has appeared at the potential more negative than -0.5 V vs SCE and reached its maximum at about -0.8 V. When the applied potential was set back to 0.0 V the absorption band disappeared. Therefore this absorption measurement in Zr-VP films is reversible with an applied potential. The absorption spectra of Zr-EPPI film are shown in Fig. 2(right). The bands at λ_{max} of 500 nm correspond to the absorption band of unreduced Zr-EPPI film and the bands at λ_{max} of 510 nm to that of the reduced one at -0.8 V cs SCE. The changes between absoprtion bands of the unreduced and reduced ones are also reversible with the applied potential 0.0 and -0.8 V vs SCE. As the number of Zr-VP and Zr-EPPI layers on TiO_2 film increases the corresponding absorption band has also systematically increased as shown in Fig. 2. This is consistent with the result of cyclic voltammograms.

In summary this study has shown that mutilayers of Zr-VP and Zr-EPPI can be prepared on nanoporous TiO_2 film electrode via recently established sequential adsorption method of metal phosphonate multilayers for the first time. The surface defect sites of Ti^{4+} on TiO_2 allows the direct coordination of phosphonate functional group of the compounds without any anchoring layer which is usually needed in this technique. The heterogeneous electron transfer from the conduction band of TiO_2 to the Zr-VP and Zr-EPPI multilayers has been observed by cyclic voltammetry and spectroelectrochemical method. We are currently investigating the possibilities of electrochromic devices using these redox couple multilayers.

AKNOWLEDGMENT

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