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Electrochemical-Assembly Approach to Nano-Ordered Conducting Polymer Films

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ECA (electrochemical-assembly), a new method for preparing nano-ordered conducting polymer films is reported A nano-ordered conducting film of polyaniline / *p*-aminothiolphenol (PANI/PATP) is constructed by this new technique. The properties, structure and surface topography of the polymer film of PANI/PATP are investigated by surface enhanced Raman scattering (SERS), scanning tunneling microscopy (STM) and cyclic voltammetry. The results indicate that the close packed PANI/PATP film is flat, uniform and ordered.

Keywords: electrochemical-assembly; *p*-aminothiolphenol; polyaniline; nano-ordered conducting polymer films

INTRODUCTION

The nano-ordered conducting polymer films of PANI/PATP prepared by the electrochemical-assembly technique is reported in this paper. The PATP monolayer was first self-assembled onto gold surface. Then electrochemical polymerization of PATP and aniline was carried out by programmed potential pulses

EXPERIMENTAL SECTION

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Materials

Reagent-grade PATP obtained from Sigma Chemical Company, was used without further purification. Ethyl alcohol absolute as well as other regents were analytic-grade.

Film Preparation

After appropriate surface treatment, PATP monolayers were formed[1]. Then, a ultra-thin film of PANI, which was about 2 nm in thickness, was deposited under programmed potential pulses with the potential of −0.2 to 0.9 V and width of 0.1 s in the solution of 1.0 mM aniline + 1 M H_2SO_4. The electrode was rinsed with a large volume of deionized water, dried with N_2 gas.

Apparatus

A confocal microprobe Raman system (LabRam I, Dilor), a NonoScope II scanning tunneling microscope (Digital Instruments) and a computer controlled electrochemical workstation (Model 660, CH Instruments) were used for SERS, STM and voltammetry measurements, respectively.

RESULTS AND DISCUSSION

SERS spectrum of PATP and PANI/PATP

The normal Raman spectrum of solid PATP (powder) as well as the SERS spectra of PATP and PANI/PATP polymer adsorbed on the electrochemically roughened bulk gold surface are shown in Figure 1.

Figure 1a is significantly different from Figure 1b. The changes in peak frequencies and relative intensities are remarkable. In addition, the S-H stretch at 2576 cm^{-1} observed in the normal Raman spectrum of solid PATP was loss in the SERS spectrum of PATP/Au (not shown). These results indicate that PATP adsorb onto the gold surface via the S atom. Moreover, the selective and large enhancement only of the four b_2 modes (8b, 19b, 3, 9b), which was explained in terms of the CT mechanism in the report of Osawa[2], shows that adsorbed PATP molecules take a standing-up orientation on gold surface.

In Figure 1c, the bands at 1383 and 1358 cm^{-1} are assigned to C-N stretch of radical cation of N-N′-diphenyl-1,4-benzenediamine ($BBB^{\bullet\oplus}$)[3]. The bands at 1628 and 606 cm^{-1} are the key bands for the participation of *p*-disubstitude benzene rings in polymer chain. The results indicate that polymerization of aniline

and PATP occurred. The remarkable decrease of the band at 1077 cm^{-1} is attributed to the C-S stretch of PATP covered by the PANI.

STM images of PATP and PANI/PATP

STM image of the PATP/Au(111) shows ordered line arrays or herringbone structure, which comprise particles (the bright spots) with mean particle-size 5 nm (Figure 2A). Comparing the size of PATP molecules with the bright spots, it is assumed that approximately 11 molecules of the adsorbed PATP have clumped a "molecules cluster" at the early stages of adsorption.

STM image of PANI/PATP/Au (Figure 2B) reveal that it is a close-packed nano-ordered film with the same mean particle-sizes as the PATP/Au (Figure 2A). Furthermore, it is shown that the surface topography of PANI/PATP/Au is flatter and more uniform than PATP/Au monolayer.

Electrochemical behaviors of PATP and PANI/PATP

Figure 3 shows the cyclic voltammograms of bare gold (dot line), PATP/Au (dash line) and PANI/PATP/Au (solid line) in 0.01 M $K_3[Fe(CN)_6]$+0.5 M KNO_3 aqueous solution. It can be observed that both PATP/Au and PANI/PATP/Au exhibit high current responses in $[Fe(CN)_6]^{3-}$ solution. In addition, the current response of PANI/PATP/Au is close to the one of bare gold, indicating that this nano-ordered polymer film have excellent electron transfer performance. This is consistent with the SERS evidences of the presence of the $BBB^{\bullet\oplus}$.

CONCLUSION

Electrochemical-assembly is a simple and convenient method of preparing well-order monolayers for its combing the advantages of ordered adsorption and controlled electropolymerization. Different from SAMs, fast electron transfer is characteristic of electrochemical-assembled monolayers. The chain length of the oligomer film can be controlled easily by the polymerization charges. There is no necessary for preparing the target molecules in advanced. The film prepared by electrochemical-assembly is expected to be ideal substrates for depositing semiconductor ordered nanoparticles.

Acknowledgments

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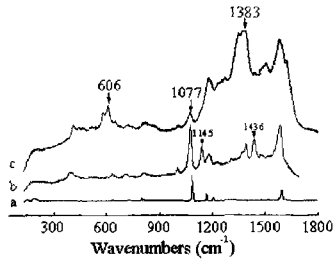

FIGURE 1 Normal Raman spectrum of solid PATP (a), SERS spectrum of PATP (b) and PANI/PATP polymer film (c) on Au. Excitation line: 632.8 nm.

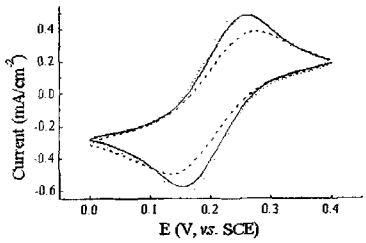

FIGURE 3 Cyclic voltammograms of a bare Au (dot line), PANI/PATP/Au (solid line) and PATP/Au electrode in 0.01M $K_3[Fe(CN)_6]$ + 0.5M KNO_3 aqueous solution. Scan rate: 100 mV/s.

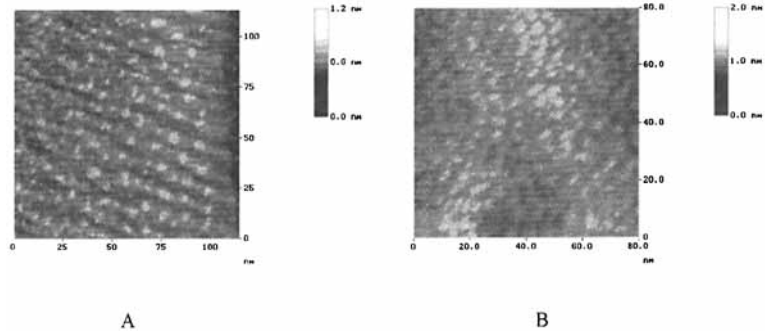

FIGURE 2 STM images of a PATP monolayer adsorbed on Au (111) surface (V_b = 50 mV, I_t = 400 pA) (A) and a PANI/PATP polymer film electro-polymerizated on Au (111) surface (V_b = 20 mV, I_t = 1.556 nA) (B) in constant current mode.

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