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Applications of scanning probe microscopy in intrinsically conducting polymer research

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Abstract The applications of scanning probe microscopy (SPM) in intrinsically conducting polymer research is briefly reviewed, including morphology observation, nanofabrication, microcosmic electrical property measurements, electrochemistry researches, in-situ measurements of film thickness change, and so on. At the same time, some important variations of SPM and the related techniques are briefly introduced. Finally, the future development of SPM in the study of intrinsically conducting polymers is prospected.

Keywords scanning probe microscopy, intrinsically conducting polymer, review

1 Introduction

Intrinsically conducting polymers (ICPs) [1] have wide application prospects in different fields, such as energy, information, electronic devices, chemical and biological sensors, electromagnetic shielding, and metal anticorrosion, etc. Scanning probe microscopy (SPM) uses a tiny probe to scan sample surface to get the sample surface morphology as well as the interaction information between the probe and the surface. SPM has the advantages of high resolution (attaining atomic level), simple specimen preparation, less limitation by the working environment, and various functions (multiple operation mode), etc. Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) are the two most familiar forms of SPM. STM with atomic level resolution, invented by Binnig and his co-workers [2], can be used to investigate the atoms' structure and their properties on a solid conducting

specimen surface. However, STM characterization requires that samples should be electrically conductive, which limited its application in semiconductor and insulator sample measurements. This problem was solved with the invention of AFM in 1986 [3]. AFM not only observe the surface morphology of insulator with approximately atomic resolution, but also measure the elasticity, plasticity, hardness, friction, and other mechanical properties of the surface [4]. In addition to the morphology observation and microscale material properties measurements, SPM is especially useful in nanofabrication. This article briefly outlines the various applications of SPM in intrinsically conducting polymer research.

2 Study on surface morphology and structure of conducting polymers

Conducting polymer films are usually formed on the substrate by electropolymerization or spin-coating. It is of great importance to carry out STM and AFM characterization on surface morphology and microstructure of thin films [5–7].

Some reports have shown that globular form is a typical micro-scale morphology of electrochemically synthesized polyaniline films [5,6]. There are two kinds of nucleation, namely instantaneous and progressive, and two types of growth: two dimensional (2-D) and three dimensional (3-D), in the electrochemical growth of conducting polymers. The number of nuclei in the instantaneous nucleation is constant, and they grow on their former positions on the bare substrate without the formation of new nuclei. Hence the radii of the nuclei are larger and the surface morphology is much rougher. In the progressive nucleation, the nuclei grow not only on their former position on the bare substrate but also on the newly formed small nuclei particles, and the resulting surface morphology is much flatter. In the 3-D growth, the growth rates of nuclei are essentially equal or comparable in the direction parallel or perpendicular to the electrode surface. However, in the 2-D growth, the nuclei grow more quickly in the parallel direction than the perpendicular direction. From the comparison of Fig. 1a and 1b, it can be seen that: when the polymerization time is 0.025 s, the growth rates of nuclei are faster in the direction parallel to electrode surface than that to

Translated from *Chinese Journal of Applied Chemistry*, 2006, 23 (2) (in Chinese)

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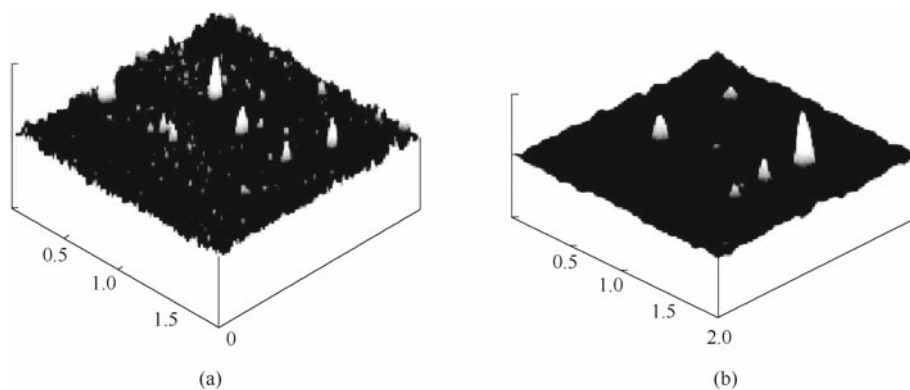


Fig. 1 AFM images of polyaniline on HOPG in a 0.02 mol/L aniline/0.04 mol/L sulfuric acid solution [8]. Polymerization time: (a) 0.025 s, (b) 0.050 s

the perpendicular direction, and the number of nuclei is little. When the polymerization time is 0.050 s, the growth rates are essentially comparable in the directions parallel and perpendicular to the electrode surface, and the number of nuclei is significantly increased. Therefore, the polyaniline film is in the 2-D growth when the polymerization time is 0.025 s, and in the 3-D growth when the time is 0.050 s [8]. Conducting polymers, such as polyaniline and polypyrrole can be used to immobilize galactose oxidase. Characterization of surface morphology with STM can detect whether galactose oxidase is doped into the conducting polymer film [9].

SPM investigation has shown that the globular particle form is also the primary surface microstructure of polypyrrole films [10–12]. As the doped polypyrrole films have electrical conductivity, STM can be used directly to investigate its local surface morphology. At the same time, the influence of the applied electrochemical potential on surface morphology can be investigated by in situ EC-AFM. For example, Froeck et al. [11] have used STM and AFM to examine the surface properties of polypyrrole films prepared under different electrochemical conditions. Their results show that the surface morphologies of polypyrrole films synthesized under different current densities are different. High current densities result in a rough film surface, while a smooth and compact film surface can be obtained under low current densities. Under electrochemical potential controlled conditions, the surface roughness increases when the anodic potential is also increased. The conclusions from Czajka's STM results show that: the polypyrrole films prepared electrochemically on HOPG exhibit disordered non-crystalline structure; the polypyrrole surface corrugations and the dimensions of the glucose oxidase molecule are of the same order of magnitude, allowing strong adsorption of the enzyme to the conducting polymer [13].

In situ electrochemical SPM measurements can be used to study the surface morphology changes of the conducting polymer films [7,12]. For example, the morphology changes of the polypyrrole films on platinum, glass carbon, and gold electrodes during electrochemical synthesis and oxidation–reduction processes have been investigated by Compton

et al., using in situ electrochemical AFM [14]. It was found that the morphology of polypyrrole in the initial stage of synthesis depends on the nature of electrode; the supporting electrolyte affects the kinetics of the synthesis process, and after synthesis, morphology of the polypyrrole film changes with time.

STM study shows that the polythiophene films also have the typical particle morphology of the conducting polymer [7]. Using AFM, Levi et al. [15] confirm that particle form is the primary morphology of the polythiophene film deposited on the platinum microelectrode. Because of the rigid property of polythiophene molecule chains, there are great research interests in the study of the morphology of polythiophene single molecule chain. STM has become a useful tool in this research field due to its super-high resolution [16–18]. Fig. 2 is a high resolution STM image of a polythiophene molecule chain with side chains on its backbone.

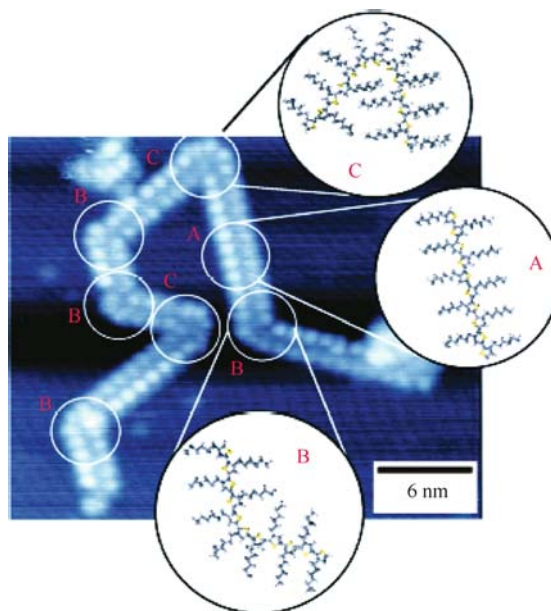


Fig. 2 STM image of thiophene polymer on Cu(111) substrate [16]

There are also some reports on the patterned surfaces of polythiophene films observed by SPM [19,20]. For example, AFM and LFM (lateral force microscopy) were used by Asmus et al. to study the patterned surface structures of two types of the conductive polythiophenes [20]. Because the surface friction between the ion treated area and the untreated area is different, the patterned region with sharp contrast can be observed in LFM image. In addition, SPM technique was also used to study the microstructures of other conducting polymers, such as phthalocyanine [21].

3 Nanofabrication of conducting polymers

With the development of SPM and nanotechnology, the probe of SPM can be used to induce the polymerization of conducting polymers on the substrates or to modify the substrate surface with conducting polymers. Local electropolymerization of conducting polymers explored with STM on selected region depends on the driven force provided by STM tip. For example, Penner et al. electropolymerized aniline on nano-scale regions of a graphite substrate by applying bias voltage pulse between STM tip and sample surface, obtaining the polyaniline nanoparticles [22].

A scanning or oscillating AFM tip, providing the horizontal scratching force and the vertical tapping force, is essential as the driving force for the surface modification with the conducting polymers. For example, Maynor et al. used the AFM tip as a “nano-pen” and fabricated polythiophene nanowires on the semiconducting and insulating surface through Electrochemical Dip-Pen Nanolithography [23]. Cai et al. carried out the localized electropolymerization in a selected area and produced the nanomodification of lines, square platforms, or hollows of polyaniline and polypyrrole on the substrates [24].

Moreover, AFM can also be used to move or cut off the conducting polymer wires. For example, using STM and AFM, Ito et al. observed the complex molecule wires formed by polyaniline with β -cyclodextrin and α -cyclodextrin nanotubes [25,26]. And, they manipulated the complex molecule wire formed by polyaniline and α -cyclodextrin nanotubes with AFM tip in contact mode [27]. The molecule wire is moved at the lower AFM tip loading force and cut off by a higher loading force. Also, the scanning electrochemical microscopy (SECM), a newly developed scanning probe technique, was utilized in the fabrication of conducting polymer microstructures [28]. The driving force for the modification of substrates processed with SECM was provided by the electrode of SECM.

4 The electrical properties of conducting polymer surface

Owing to its small tip radius, SPM is also an ideal tool for the local electrical investigation of conducting polymer. For

example, Liao et al. obtained the current map of the conducting interpenetrating polymer networks (IPN) using STM. It was shown that the conductive region of the doped polyaniline was distributed as continuous conductive networks in the matrix, which resulted in higher conductivity and low threshold concentration of doping for the conductive IPN [29]. Dietler et al. investigated doped polypyrrole by a combination of STM and AFM [30]. They observed the existence of domains with different conductivities on the sample surface when they imaged the surface morphology.

In addition, electrostatic force microscopy (EFM) also can be used to characterize the electrical properties of conducting polymers. Barisci et al. investigated the surface potential distribution of polypyrrole films in nanoscale using AFM and EFM while they characterized the surface morphology [31]. From the comparison of topography image and surface potential (SP) image, it was shown that SP distribution is not uniform, the top of the polypyrrole grains exhibits consistently low SP with respect to the surrounding areas, suggesting that the polymer grains are more oxidized and therefore, more doped than the peripheral regions, and possessing higher conductivity. The dispersion of SP also implies that the redox potential of the polymer does not have a well defined and unique value at the microscopic scale. Therefore, the redox potential of material is in reality an average of many closely distributed values.

5 The application of conductive AFM

The conductive AFM (the AFM equipped with a conductive probe) possessing the advantages of AFM and STM and overcoming their shortages can be used conveniently to measure the conductivity of conducting polymers, especially for getting their current–voltage (I – V) characteristics. For example, vertical direction I – V characteristics of polypyrrole nanotube deposited on Au were measured by Park et al. using a metal coated tapping-mode AFM tip [32]. Using vertical electrode configuration, the conductive SPM tip used as one electrode and Au evaporated on SiO₂ substrate as another one, linear I – V characteristics were observed.

6 In situ study of the thickness changes of conducting polymers

SPM can be used to follow in situ thickness changes of conducting polymer films at the nanoscale. This method is based on the assumption that the piezo of the SPM will follow a thickness changes of the polymer film if the distance between the polymer film and probe is kept constant during the experiment, that is the piezo will shrink or swell following the swelling or shrinking of the polymer film. For example, Skompska et al. [33] reported that the redox process of poly(3-hexylthiophene) is accompanied by significant changes of the polymer film thickness, as investigated by in situ

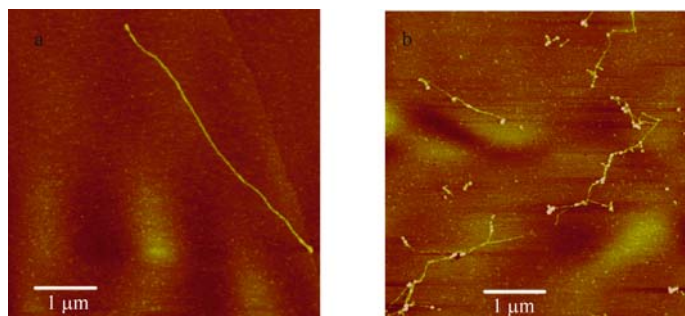


Fig. 3 AFM images of (a) aniline-DNA complex nanowire formed by treating the DNA template with 500 nmol aniline, (b) PANI-DNA nanowires formed on mica surface with aniline-DNA complex nanowires as precursor [34]

EC-AFM. The thickness of poly (3-hexylthiophene) film increases with the increase of the scanning potential during the doping process and decreases when the potential is decreased during the dedoping process. But the change in the film thickness is very slow and remarkably delayed with respect to the changes of the scanning potential.

7 Electrochemistry of conducting polymer

That electropolymerization of the monomers of conducting polymer on the substrate surface can be induced by the SPM tip and has been mentioned intensively in the previous parts of this article [22–24]. Furthermore, the EC-AFM prepared by equipping the original AFM with an electrolytic cell, a potentiostat and the corresponding software can be used to simultaneously obtain cyclic voltammograms of conducting polymer films. For example, with in situ EC-AFM, Skompska et al. obtained cyclic voltammograms of poly (3-hexylthiophene) film besides that they observed its thickness changes during the redox process [33].

8 Nanocomposites based on conducting polymers and biomolecules

A novel and useful way to fabricate nanostructured materials is to imitate the rich and delicate structures of biological samples in nature. DNA, a biological macromolecule, due to its unique electrostatic and topographic properties (only 2 nm in diameter), is an ideal biological template for construction of nanomaterials. In our group [34], we first incubated the negatively charged linear DNA molecules with the protonated aniline in solution for a certain time so that aniline assembled on DNA, so the DNA-aniline complexes were formed. With the tapping mode, the uniform and smooth complex nanowire can be observed by AFM (Fig. 3a). After polymerization of the aniline on the DNA, the DNA-templated polyaniline nanowires were produced (Fig. 3b). Our strategy effectively avoided the non-specific binding of aniline on the substrate, which resulted in the clear backgrounds in our AFM images.

9 Outlook

There is great development potential of conducting polymers in fields, such as microelectronic device and nanotechnology. Therefore, nanofabrication of conducting polymer on the microscale and nanoscale; as well as, construction of various conducting polymer nanomaterials with novel structures will be highlighted and concentrated in the research and application of conducting polymer. So, development of a real time, in situ, and higher resolution scanning probe technique and the SPM based on the nanofabrication will show much potential applications in the field of conducting polymer.

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