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Determination of fractal rough surface of polypyrrole film: AFM and electrochemical analysis

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ABSTRACT

Physico-chemical properties of conductive polymers depend on the morphology and characteristic of the synthesized film which emerge from synthesis conditions. For example, conductivity of polypyrrole is related to the fractal dimension of surface. Atomic force microscopy (AFM) is a powerful technique in revealing characteristic of surfaces. In the present research electrochemical techniques and atomic force microscopy are employed to analyze the surface morphology and parameters of surface such as interface width, kurtosis, Hurst exponent, fractal dimension and lateral correlation length for polypyrrole electrodeposited on glassy carbon (GC) electrode and relation between skewness and kurtosis were investigated. Height–height correlation function shows the correlation of heights in different points on the surface and can be calculated by analyzing AFM data and surface profile. Scanning electron microscopy (SEM) analysis carried out to confirm the AFM results. Cyclic voltammetry and electrochemical impedance spectroscopy methods are used to compare the electrochemical capacitance of films with different roughness. AFM images were used to estimate the surface area and results showed that the films synthesized in higher temperatures are rougher and have a larger surface area and according to the results of electrochemical experiments rougher surfaces with higher skews have larger electrochemical capacitance. The study of surface morphology and physico-chemical properties of polypyrrole film can provide suitable methods of synthesis of films with required properties.

1. Introduction

The surface analysis of thin films is one of the most interesting fields for investigation in surface science. When thin films are deposited on a substrate, different conditions of experiment during the deposition process may affect the surface morphology of the film [1,2]. Different temperatures during deposition will lead to surfaces with different roughness and the resulting film may have different properties. Conducting polymers are interesting materials that their surface roughness highly affects their properties such as electrochemical and conductive properties. Among the conducting polymers, polypyrrole (PPy) is one of the most promising materials for many potential applications such as fuel cells [3,4], solar cells [5–7], batteries [8–10], sensors [11–13] and so on, because of its high electrical conductivity and environmental stability. Changing the temperature of synthesis highly impresses the surface morphology of PPy. For investigation of this effect, PPy film was deposited on the glassy carbon (GC) electrode in various synthesis temperatures and then the atomic force microscopy method was used to analyze the PPy film. Atomic force microscopy (AFM) is one type of scanning force microscopy (SFM), which uses different kinds of intermolecular forces as the detection signal to achieve the measurement of different physical properties of a surface in nanometer scale [14]. AFM measurements on (very) rough surfaces must be represented with three dimensional surface rather than top-view projections. This is necessary for the assessment of quality and detection of possible artifacts in some regions of the image by tip–sample convolution or tip imaging [15]. An AFM image is a simulated image based on the height of each point of the surface and in fact each point (x, y) of the surface has a height $h(x, y)$ [16]. According to height distribution and height difference between different areas of surface accurate information about surface roughness can be calculated.

Cyclic voltammetry and electrochemical impedance spectroscopy was used to analyze the effect of surface roughness on the electrochemical capacitance of PPy film and comparing the values of capacitances in different synthesis temperatures. Investigation of PPy surface has been reported in literature. For example in 1998 Silk and colleague studied the surface morphology of PPy by fractal dimension analysis using AFM method [17]. In 2004 Zhou and

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colleague reported a detailed investigation of the effects of experimental conditions on the ultimate patterns of the PPy films on self-assembled monolayer patterned silicon and gold substrates [18]. In 2006 a greener method was introduced by Rasika Dias and colleague for the high quality PPy and the properties of PPy was studied by scanning electron microscopy (SEM) and impedance spectroscopy [19]. Also in our previous work in 2012, fractal dimension and anomalous diffusion in PPy film was studied using cyclic voltammetry, impedance spectroscopy and AFM methods [20]. A lack of statistical analysis of surface of conducting polymers – specifically for PPy – exists in literature. We tried to statistically analyze the surface of PPy film and relate the statistical results to the electrochemical properties of the conducting polymer. In this research, roughness parameters such as interface width, skewness, kurtosis, Hurst exponent, and lateral correlation length are used to study the PPy surface. The electrochemical capacitance of PPy film in different synthesis temperatures also are compared by electrochemical methods.

2. Experimental

Chemical materials Pyrrole (C_4H_5N) and potassium perchlorate ($KClO_4$) used in this work were of Merck origin. Pyrrole was distilled before use, but $KClO_4$ was used without further purification. All solutions were prepared in doubly distilled water. All electrochemical measurements were carried out in a conventional three electrode cell powered by a potentiostat/galvanostat (EG&G, 273A) and a frequency response analyzer (EG&G 1025). The system was run by a PC through M270 and M398 software via a GPIB interface. The frequency range from 100 kHz to 10 mHz and modulation amplitude of 5 mV were employed in impedance studies. The experiment cell was kept at the required temperature by means of thermostated water bath. Electropolymerization and subsequent electrochemical studies were carried out in a conventional three electrode cell with a GC electrode having an exposed circular area of 3.14 mm^2 was employed as the working electrode and its potential monitored against a saturated calomel electrode (SCE). A platinum plate formed the counter electrode. All data fittings were performed using MATLAB software and equivalent circuit was obtained from Zview software. The AFM images were recorded on a NanoScope II® from Digital Instruments, USA in Contact mode using Si_3N_4 Tips. NanoScope and MATLAB software were used for analyzing AFM data. PPy films were prepared by chronocoulometry method in 0.5 V vs. SCE with total charge of 40mC for each film in an aqueous solution containing 0.1 M of PPy monomer and 0.1 M of $KClO_4$. After depositing polypyrrole on GC electrode the cyclic voltammetry and EIS measurements were performed in an aqueous solution containing 0.1 M of $KClO_4$.

3. Results and discussion

3.1. AFM studies

Each surface can be considered such a $N_x \times N_y$ matrix that each (x_i,y_j) array of this matrix has a height of $h(x_i,y_j)$[21]. The height of each point on a rough surface can be obtained from one of the scanning probe microscopy (SPM) methods such as AFM and then these heights can be embedded in matrix A1:

$$A1 = \begin{bmatrix} h(1,1) & \dots & h(1,N_y) \\ \vdots & \ddots & \vdots \\ h(N_x,1) & \dots & h(N_x,N_y) \end{bmatrix} \tag{1}$$

The surface profile can be obtained from this matrix in a three dimensional plot (Fig. 1).

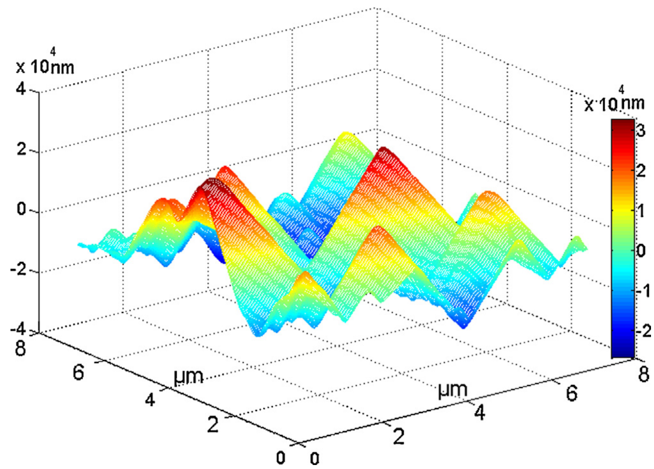

Fig. 1. Surface profile of PPy synthesized in 45 °C.

In the present work we use AFM images with matrixes having 256 rows and 256 columns which give the height of 65,536 points. Due to a large number of points we employed the statistical analysis to investigate the surface. In order to calculate roughness parameters we need the value of average height that can be obtained from the relation:

$$\bar{h} = \frac{1}{N}\sum_{i=1}^{N} h_i \tag{2}$$

where N is the number of points and h_i is the height of ith point.

3.2. Roughness parameters

In the following sections, roughness parameters are introduced and the values of them are calculated in different conditions.

3.2.1. Interface width

Interface width w or root mean square (RMS) roughness is the standard deviation of height of surface [22]. The w describes the fluctuations of the surface height around an average surface height. The rougher surface has the larger w. The w can be calculated from following equation:

$$w = \left[\frac{1}{N}\sum_{i=1}^{N}(h_i - \bar{h})^2\right]^{1/2} \tag{3}$$

The w is in units of length (Appendix).

In this research four different surfaces of PPy film were investigated that was synthesized in different temperatures. AFM images with 8 µm × 8 µm scan area were taken from ten different randomly selected areas of the surface of PPy in each temperature. The values of w in Table 1 show that the higher temperature forms a surface with larger w. The rougher surfaces were synthesized in higher temperatures. Fig. 2 shows a typical AFM image synthesized in different temperatures.

3.2.2. Skewness and kurtosis

Skewness (S) is a parameter that shows the surface that has more holes or bumps. The value of S can be obtained from the relation:

$$S = \frac{1}{w^3}\frac{1}{N}\sum_{i=1}^{N}(h_i - \bar{h})^3 \tag{4}$$

Skewness is a dimensionless parameter that the sign of it, positive skewness or negative skewness reveals that the further points