Vacuum 114 (2015) 17–20

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Rapid communication

Diffusion through the self-affine surface of polypyrrole film

Ahmad Sharifi-Viand [a], Mohammad Ghasem Mahjani [b,*], Reza Moshrefi [a], Majid Jafarian [a]

[a] Department of Chemistry, Faculty of Science, K. N. Toosi University of Technology, P. O. Box 15875-4416, Tehran, Iran
[b] The Center for Complex Systems Research, K. N. Toosi University of Technology, P. O. Box 15875-4416, Tehran, Iran

ARTICLE INFO

Article history:
Received 29 October 2014
Received in revised form
20 December 2014
Accepted 30 December 2014
Available online 7 January 2015

Keywords:
Fractal dimension
Self affinity
Anomalous diffusion
Polypyrrole

ABSTRACT

The fractal dimension of the surface of Poly Pyrrole (PPy) film was calculated using Atomic Force Microscopy (AFM) images, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) methods. The results obtained by electrochemical methods showed more chaotic behavior than the AFM image because some parts of porous structure were not accessible to imaging devices. Since the values obtained from electrochemical methods are based on a diffusing process, comparing the values of fractal dimension obtained from SEM images and electrochemical methods showed that a diffusing process through the PPy film presents self-affine scaling property.

Diffusion through the self-affine fractal surface of PPy film has been investigated in this research. Sharifi-viand et al. already reported anomalous diffusion in PPy film [1]. Anomalous diffusion results from processes in which particles are trapped in porous media. In this case the relation between displacements of particles and diffusion time deviates from an exact $t^{1/2}$ power low and the power exponent is lower than 1/2 [2]. The roughness of the surface causes trapping of the diffusing particles in the holes and they spend more time than usual to diffuse through the surface. This is due to the unusual geometry of the polymer surface i. e. fractal geometry. Several methods are available to investigate fractal surfaces and calculate fractal dimensions. In this work electrochemical methods and AFM images are used to study the fractal surface of a PPy film. When the value of fractal dimension is equal to 2 the surface is totally smooth. When this value is equal to 3 the surface is completely rough and jagged. An increase in the value of fractal dimension between 2 and 3 results in an increase of the surface roughness and complexity of the surface (higher dimension) [3]. Pyun at al showed that diffusion towards self-affine fractal surfaces has self-similar scaling property [4]. Diffusion in conducting polymers due to high porosity of surface structure shows anomalous behavior. In this work we attempt to show whether the diffusion through the self-affine surface of PPy film is self-similar or self-affine. At first step the self-affine fractal dimension, D_{sa}, and apparent self-similar fractal dimension D_{ss} were calculated by perimeter-area and triangulation methods, respectively, using AFM images and then the fractal dimension related to the diffusion was determined by cyclic voltammetry (D_{CV}) and was confirmed by EIS method (D_{EIS}). Afterwards the values obtained from electrochemical methods which are related to the diffusion process were compared with the values calculated from AFM images.

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. In order to preparing the PPy film glassy carbon (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. The GC electrode was immersed in a solution of 0.1 M of $KClO_4$ and 0.1 M of pyrrole monomer at the room temperature and the electrode potential was cycled with the scan rate of 50 mV/s for 5 cycles. This modified electrode was investigated in a 0.1 M of $KClO_4$ by CV method with different scan rates and EIS measurements was carried out on the same solution using the peak current potential. AFM images were recorded on a NanoScope II® from Digital

* Corresponding author. Tel.: +98 21 22853551; fax: +98 21 22853650.
E-mail address: mahjani@kntu.ac.ir (M.G. Mahjani).

http://dx.doi.org/10.1016/j.vacuum.2014.12.030

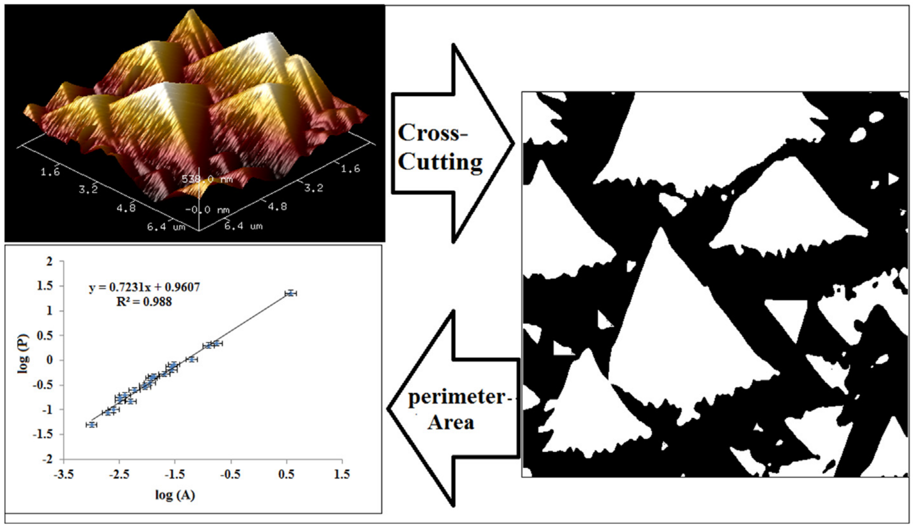

Fig. 1. An AFM image of PPy film prepared by CV on GC electrode (top left) AFM image cross-cut up to a height corresponding to 45% of the maximum height (right) and log (P) vs. log (A) plot for the lakes generated by the cross-cut image (down left).

Instruments, USA in Contact mode using Si_3N_4 Tips. NanoScope and MATLAB software were used for analyzing AFM data.

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). For a three-dimensional image D_{ss} and D_{sa} can be calculated by triangulation and perimeter-area methods respectively.

AFM images of ten different 7.5 μm × 7.5 μm areas of the film surface were used to calculate the D_{sa} and D_{ss}. An AFM image of the surface of the prepared PPy is shown in Fig. 1. In order to calculate the self-affine fractal dimension D_{sa} the perimeter-area method is used. For using this method a cross-cutting of the surface should be used. The perimeter P (edge of lakes) and the area A (black pixels) of each resulting lake (Fig. 1 right) are useful to calculate the D_{sa}. Plotting log (P) vs. log (A) results a line with the slope of $(D_{sa}-1)/2$ [5]:

$$\log\left(P\right) = \left(\frac{D_{sa}-1}{2}\right)\log\left(A\right) + C \quad (1)$$

where C is a constant. The threshold of cross-cutting of the AFM image was selected up to heights corresponding to 20%, 45%, 65%, and 80% of the maximum height and the values of D_{sa} were 2.46, 2.44, 2.41 and 2.44, respectively and the average value is 2.44 ± 0.02. Plot of log (P) vs. log (A) for the AFM image cross-cut up to a height corresponding to 45% of the maximum height is shown in Fig. 1(lower left).

For calculating the D_{ss} in the first step the image is embedded in a square with side length of L. Hence four new points can be found corresponding to each vertex according to the height of those points (Fig. 2). By connecting new points two triangles will be created (*ΔABC* and *ΔADC*). The first estimate of the surface area SA is the sum of the area of these two triangles. In the second step the image is divided to 4 squares and 8 triangles are created. The side of the square in this step is L/2. In step N the image is divided to N^2

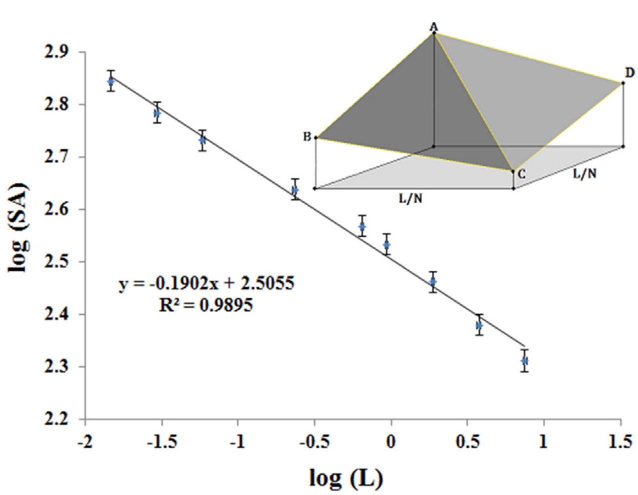

Fig. 2. A schematic of triangulation by four points in an AFM image and log (SA) vs. log (L) plot for triangulation of an AFM image of a PPy film.

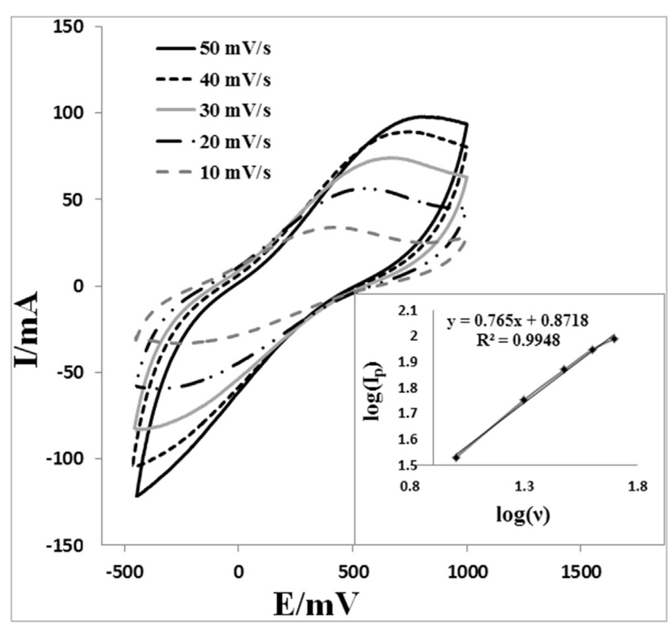

Fig. 3. Cyclic voltammograms of a PPy surface in different scan rates and respective log (I_p) vs. log(ν) plot for cyclic voltammograms.