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The effect of heat treatment on the surface structure of polyaniline nanostructured film: An experimental and molecular dynamics approach

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ABSTRACT

The influence of drying temperature, T on the surface structure of polyaniline (PANI) nanostructured films dried at temperatures less than the glass transition temperature, T_g and between T_g and melting temperature, T_m was investigated by atomic force microscopy (AFM) and ZeScope optical profilometry. The expected power law behavior associated with surface roughness over small length scales was confirmed at different drying temperatures. To correlate the value of the film thickness determined based on AFM with that obtained from ZeScope measurements, a model of height correcting factor is introduced. The variation in saturated roughness of the PANI film was determined to follow a power law model in the range of $T<T_g$, with a saturated roughness exponent of 4.48 ± 0.4. The structure of the PANI film has been investigated based on molecular dynamics simulation. The applicability of power law model was confirmed by simulations, based on which the saturated roughness exponent was determined to be 4.90 ± 0.5.

1. Introduction

Semiconducting polymers represent a new and exciting field of research, which lies at the boundary between chemistry and condensed matter physics. Study of semiconducting polymers addresses several theoretical questions of enormous interest and opens the possibility for several important technological applications in a wide variety of fields such as batteries, antistatic films, gas sensors, organic light emitting diodes (OLEDs), organic display panels and solid-state dye-sensitized solar cells (DSSCs) [1–5].

Among semiconducting polymers, the members of the polyaniline (PANI) family have received considerable attention in the past few years because of their remarkable properties. The world scientific community recently recognized the potential importance of PANI when Shirakawa, Heeger and MacDiarmid were awarded the 2000 Nobel Prize in Chemistry for their research on this polymer [6]. The semiconducting properties of PANI can be modified so that it exhibits a reversible behavior either as an insulator or as a conductor depending on the characteristics of their repeat units.

Recently, researches have focused on the combination of PANI and TiO_2 to improve their electronic conductivity and solar energy transfer [7–10]. Mo et al. [8] synthesized PANI–TiO_2 by in situ polymerization of aniline, and found that the prepared nanocomposite showed higher dielectric constants. Li et al. [9] prepared nanoparticles of PANI–TiO_2 by chemical oxidative polymerization, and found that PANI–TiO_2 composite showed higher photoelectric catalytic activity than that of pristine TiO_2 under visible light irradiation. Wang et al. [10] prepared PANI–TiO_2 film using the sol–gel method followed by a facile chemisorption, and found the photocatalytic activity and photoelectrocatalytic oxidation of the PANI-modified TiO_2 nanoparticles were improved remarkably. In the system of PANI–TiO_2, an electron can be added to the conjugated polymer backbone by a chemical reduction or n-type doping, or be removed by chemical oxidation, or p-type doping [11]. Based on this, the PANI–TiO_2 system could be also useful as an adhesion promoter and corrosion inhibitor because PANI, being p-type with band gap of 2.1 eV [12], provides a large barrier for electron transport while TiO_2, being n-type with a band gap of 3.13 eV [13], causes an obstruction against hole transport across the interface.

An important characteristic of PANI is the relative ease with which it can be processed as a film. This polymer can be formed using several methods such as the dipping or spin-coating methods at fairly low temperatures [14]. A variety of shapes including

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asymmetric and symmetric porous hollow fibers, flat sheets, and films are attainable [2]. The other useful properties of PANI include the low density and the high ratio of surface area to volume associated with films of this polymer.

A considerable experimental data has been collected to characterize PANI films through measurements of electrical and optical properties such as conductivity and reflectance, as well as structural properties such as density, and surface roughness [1,2,6,14–16]. The surface roughness associated with fluctuations in the film thickness, is a significant factor characterizing the surface morphology which determines the scattering properties of the interfaces and is often specified as a root-mean-square (rms) fluctuation in the film thickness. In addition, the conversion efficiency of thin-film solar cells depends on regulating of surface morphology during the thin film deposition process. Thus given the variation in the behavior of surface roughness over different length scales, appropriate tailoring of the rms roughness is crucial [17]. Accordingly, accurate measurement of surface roughness is a critical step in the characterization of materials used for optical, electrochemical, and electrical applications [4,11].

Measurement of the surface roughness can be performed using various surface sensitive techniques, which can be categorized as contacting and non-contacting. Contacting techniques such as atomic force microscopy (AFM) and Dektak surface profiling are based on mechanical methods, while non-contacting techniques exemplified by SEM and ZeScope optical profiling are optically based. The accuracy of mechanically-based approaches, which employ a sharp scanning probe, is usually less than that of optically-based techniques [18]. Since the probe tip is not capable of penetrating voids whose cross-sectional area is smaller than that of the scanning probe tip, the measurement may not detect the actual film thickness. On the other hand, the probe tip can cause surface scratches in the polymeric film during the scanning operation [19].

The impact of film thickness and its relation to surface roughness is linked to the value of the glass transition temperature, T_g. The glass transition temperature of the surface region is typically higher than that of the bulk. For PANI thin films, however, although T_g is relatively insensitive to the film thickness, the deposition conditions such as the drying temperature can exert an influence on the rate of the polymer cross-linking and content of residual solvent within the film affect the surface structure, which in, turn change the T_g. Other workers have demonstrated that the surface interaction between PANI chains with the underlying substrate can also affect the value of T_g [20,21].

However, it is difficult to observe the surface structure of the polymeric thin films at the atomic level using direct experimental methods. Molecular dynamics (MD) simulation overcome the limitations of traditional empirical approaches and exhibited great potential for studying the physical and structural properties of the polymers [22].

In this work, the influence of drying temperature on the morphological surface structure of PANI films coated on a nanocrystalline TiO_2 substrate is investigated experimentally based on AFM analysis and ZeScope optical profilometer. In particular, the behavior of surface roughness parameters such as rms and peak-to-valley roughness is correlated with experimentally identified surface structures such as peaks and voids at drying temperatures in the $T < T_g$, and $T_g \leq T < T_m$ ranges, where T_m is the melting temperature. A scheme for height correction is employed which allows correlation of the mean value of the film thickness determined based on AFM with that obtained using ZeScope measurements. The scaling of the roughness in PANI films is shown to follow the expected power law behavior over small length scales at the given drying temperatures. The structural morphology of the PANI film will also be evaluated based on MD simulations. Specifically, surface structure predicted by simulations will be correlated with surface roughness data over the given temperature ranges. The applicability of a power law behavior to the simulated values of surface roughness parameters will also be investigated by MD simulations.

2. Experimental

2.1. Materials

Titanium tetra-isopropoxide (TTIP 99.9%), aniline, ammonium peroxydisulfate [$(NH_4)_2S_2O_8$], hydrochloric acid, 1-methyl-2-pyrrolidinone (NMP) and ethanol were purchased from Sigma–Aldrich.

2.2. Polymerization

Polymerization of 0.55 mmol aniline was carried out at room temperature for 12 h by mixing aqueous solutions of ammonium peroxydisulfate, acting as an oxidant and hydrochloric acid, which serves as the catalyst. The initial concentrations of $(NH_4)_2S_2O_8$ and HCl were 0.25 M and 0.5 M, respectively. The PANI–Cl precipitate was filtered through a Buchner funnel and washed initially with ethanol and then with deionized water. The precipitate was subsequently dried under vacuum conditions at 55 °C. Finally, the prepared Emeraldine based powder was added to the NMP as a solvent, to make a 10 wt.% solution which was stirred for 2 h at room temperature until a homogenous and stable solution with a brownish green color was obtained.

2.3. Preparation of samples

First, the precursor solution containing TiO_2 nanoparticles were prepared by the hydrolysis of the TTIP using the sol–gel method [23]. Second, ultrasonically cleaned ITO glass was used as base for the TiO_2 nanostructured film prepared by dip-coating technique. The withdrawal velocity of substrate in the precursor solution was 5×10^{-4} m s^{-1}. The same process was repeated four times and each wet sample was inserted in the oven under vacuum condition at drying temperatures of 298 and 418 K for 30 min. The mean thickness of the resulting TiO_2 films was measured to be 21 ± 8 nm using ZeScope optical profilometer. To exclude the effect of the film thickness on the surface morphology investigation, TiO_2 nanostructured films of the same thickness were prepared in the experiments. The PANI film was coated on the TiO_2 substrate by successive immersion in the polymeric solution by the dip-coating technique. The withdrawal speed of the TiO_2 substrate was 1.0×10^{-3} m s^{-1}. A heat treatment was then applied, when each wet sample was inserted in the oven under vacuum conditions at drying temperatures ranging from 298 to 418 K for 20 min. The samples were the cooled to room temperature and prepared for further analysis.

2.4. Instrumentation

In order to study the surface morphology and roughness of the PANI nanostructured films, an atomic force microscope (AFM, DME DS-95-50) was used in the experiments. Analysis of the AFM data was performed with the image analysis software package Scanning Probe Image Processor (SPIP, Image Metrology A/S, Denmark). The roughness of the films was calculated at different length scales of the AFM images with a customized extension for this program. Film thicknesses were also measured using a ZeScope optical profilometer. Thermogravimetric (TGA) analysis of prepared films was carried out using a Perkin Elmer (Model Pyris 1) thermogravimetric analyzer at a heating rate of 10 °C min^{-1} in flowing high-purity nitrogen (15 ml min^{-1}).

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