

In situ deposition of poly(1,8-diaminonaphthalene): from thin films to nanometer-sized structures

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Abstract

Chemical in situ deposition of poly(1,8-diaminonaphthalene) (p(1,8-DAN)) on conductive supports in aqueous and acetonitrile solutions was investigated using electrochemical quartz crystal microbalance (EQCM) and UV–vis spectroscopy. The resulting deposits were examined by the means of cyclic voltammetry (CV), FT-IR and Raman spectroscopy. P(1,8-DAN) was also deposited via chemical polymerization onto a porous polycarbonate membrane (PC) which served as a template for synthesis of nanometer-sized structures. The deposits of p(1,8-DAN) on PC substrate were imaged by atomic force microscopy (AFM) and the nanostructures obtained by dissolution of the template were visualized by scanning electron microscopy (SEM). The EQCM and UV–vis studies indicated that the polymer is formed both on the surface of the substrate and in the bulk of the polymerization solution. However, polymerization of 1,8-DAN in solution is delayed in comparison with deposition on the substrate. Electrochemical and spectroscopic properties of p(1,8-DAN) formed chemically closely resemble the properties of the electrosynthesized polymer. Furthermore, SEM images of p(1,8-DAN) nanostructures revealed that the polymer nanowires are formed in aqueous solutions, whereas two types of structures: nanowires and round shaped structures, not fitting to the pore size, can be obtained by chemical polymerization in the acetonitrile medium.

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1. Introduction

Throughout the last decade a considerable attention has been paid to p(1,8-DAN) due to its unique properties [1–10]. One of the most remarkable characteristics of p(1,8-DAN) is its ability to extract and form complexes with heavy metal cations (for example Ag^+ , Cu^{2+} and Hg^{2+}). This exceptional property has been explained through investigation of molecular structure of p(1,8-DAN). It has been demonstrated that the presence of free amine groups enables p(1,8-DAN) to form strong complexes with metal ions [2,4–8]. This feature has drawn the most attention since it enables a number of

practical applications for p(1,8-DAN), such as heavy metal sensors. Up till now p(1,8-DAN) has been obtained in the form of polymer films by means of electrochemical methods. As the dimension of the film surface is limited and the processability of p(1,8-DAN) is very poor it is difficult to produce a sufficient amount of polymer and to prepare the specific structures more useful for practical applications. It is well known that the coating with a layer of conducting polymer may be achieved not only by electropolymerization but also by chemical polymerization carried out in the solution or directly on substrate surface. Many chemical oxidant like ammonium peroxydisulfate (APS), ferric ions, bichromate anions are able to oxidize pyrrole, aniline and its derivatives thus initiating the polymerization process [11–15]. The chemical polymerization is also widely used method for the template synthesis of conducting polymer nanostructures [11,16–22].

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The aim of this study is to examine the process of chemical polymerization of 1,8-diaminonaphthalene (1,8-DAN) in the bulk of solution, on the solid surfaces and subsequently formation of nanometer-sized structures. The polymerization process was studied in aqueous and acetonitrile solutions and the polymer deposits were examined with a number of experimental techniques. The properties of chemically obtained p(1,8-DAN) are compared with the one formed electrochemically. The p(1,8-DAN) nanometer-sized structures, within the template as well as extracted from the polycarbonate membrane, were examined by the means of Raman spectra and visualized by scanning electron microscopy (SEM). In addition, atomic force microscopy (AFM) was applied to visualize a bare membrane and a membrane covered with p(1,8-DAN).

2. Experimental

2.1. Chemicals

All chemicals were of the highest commercially available quality: 1,8-DAN (Aldrich), ammonium peroxodisulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (Fluka, >98%), ferric chloride FeCl_3 (Aldrich, anhydrous), sulfuric acid (POCh, 96%), hydrochloric acid (POCh, 36%), lithium perchlorate LiClO_4 (Aldrich), acetonitrile (Aldrich), chloroform (POCh, reagent grade). Aqueous solutions were prepared from water of high purity (Milli-Q).

2.2. Instrumentation

The electrochemical quartz crystal microbalance (EQCM) measurements were performed by means of a QCM unit (Type M3, UELKO, Poland) combined with AUTOLAB PGSTAT 30 electrochemical unit (Ecochemie, The Netherlands). The working crystals were 10 MHz AT-cut quartz crystals evaporated with 100 nm thick layer of gold (ICM, Oklahoma City, USA) with the area of 0.21 cm^2 .

Electrochemical measurements were carried out by means of AUTOLAB using conventional three-electrode cell with Pt wire as counter electrode. All potentials are quoted versus $\text{Ag}/\text{AgCl}/1 \text{ M KCl}_{\text{aq}}$ reference electrode.

Optical spectra were recorded using a double beam UV–vis spectrophotometer (Lambda 12, Perkin-Elmer). Raman spectra were recorded with Jobin Ivon spectrometer equipped with CCD detector and micro-setup. For excitation the 647.1 nm line of Kr^+ laser was used. IR spectra were recorded with the FT-IR8400 Shimadzu spectrometer.

Commercially available Nanoscope IIIa (Digital Instruments) was used to collect the contact mode in air atomic force microscopy (AFM) images. Scanning electron microscopy images were obtained with LEO scanning electron microscope.

2.3. Materials

Polycrystalline gold electrodes (Au, 99.99%; 0.2 cm^2) used for electrochemical measurements were first cleaned by annealing in the reductive flame of the burner, then they were cyclically polarized 20 times in $1 \text{ M H}_2\text{SO}_4$ aqueous solution within the -0.3 to $+1.5 \text{ V}$ potential range at a sweep rate of 50 mV/s .

Polycarbonate filtration membranes with pore diameter of 100 nm (Cyclopore, Whatman) were used as templates in the polymer nanostructures synthesis.

Glass plates covered with indium tin oxide (ITO) were washed with acetone in an ultrasonic bath.

2.4. Chemical deposition of p(1,8-DAN)

2.4.1. Aqueous solutions

Gold-covered quartz crystals, polycarbonate membranes or ITO substrates were immersed into 2.4 cm^3 solution of 1.6 mM 1,8-DAN in 1 M HCl . Then, 0.6 cm^3 solution of $0.02 \text{ M } (\text{NH}_4)_2\text{S}_2\text{O}_8$ in 1 M HCl was added as an oxidant. After several minutes the substrates were removed from the polymerization bath, rinsed with 1 M HCl and distilled water. Au and ITO electrodes with deposited polymer films were placed in $1 \text{ M H}_2\text{SO}_4$ and studied by cyclic voltammetry or UV–vis spectroscopy. Polycarbonate membranes covered with the polymer were rinsed with acetone and dried.

2.4.2. Acetonitrile solutions

Gold-covered quartz crystals or polycarbonate membranes were immersed into the solution of 0.1 M LiClO_4 in acetonitrile (1 cm^3) containing 0.05 g 1,8-DAN. Then, 1 cm^3 of acetonitrile containing 0.1 M LiClO_4 and 0.05 g of FeCl_3 was added. After several minutes the substrates were removed, rinsed with acetonitrile and dried.

2.4.3. Isolation of nanostructures

Polycarbonate membranes with deposited polymer were dissolved in chloroform and filtered through aluminum oxide membranes (Anopore, Whatman) under reduced pressure.

2.5. Electrochemical deposition of p(1,8-DAN)

Electrodeposition of p(1,8-DAN) was carried out on Au, Pt or ITO working electrodes in a one compartment cell. A double junction $\text{Ag}/\text{AgCl}/1 \text{ M KCl}_{\text{aq}}$ was the reference electrode and a large-area platinum gauze was the counter electrode. The electrodeposition bath contained 0.01 mol dm^{-3} 1,8-diaminonaphthalene (Aldrich) and 0.1 mol dm^{-3} LiClO_4 (Aldrich) as the supporting electrolyte in acetonitrile (AN) (Fluka). The polymer film was obtained by cycling (three scans) in the potential range between -0.2 and 1.2 V at the sweep rate 40 mV/s . A detailed study on polymerization and electrochemical behavior of p(1,8-DAN) has been presented elsewhere [3,7,23].

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