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Preparation and studies of transparent conductive monolayers of multiwall carbon nanotubes on quartz and flexible polymer with the use of modified Langmuir technique

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ABSTRACT

An improved Langmuir method is described and applied to produce transparent, conductive and flexible single layer of multiwall carbon nanotubes. This paper presents properties of multiwall carbon nanotubes spread on water subphase and in a form of Langmuir–Schaefer layers on a quartz plate and on flexible polymeric foil. The results show very high homogeneity of the monolayers on a very large area obtained with the use of the proposed modified Langmuir method and indicate their relatively high radiation transmission and electrical conductivity. Laser scanning confocal and scanning electron microscopic images of the layers are presented. The microscopic visualization of the nanolayers is supported by spectroscopic studies (transmittance, photoacoustics) in the range from ultraviolet to mid-infrared. Moreover, electric measurements (current *versus* voltage characteristics) of the carbon material on the polymeric foil are presented.

The obtained results of the investigated multiwall carbon nanotubes are discussed in a view of potential application in optoelectronics.

1. Introduction

In the near future a development of electronics based on carbon compounds and carbon nanostructures will let to fabricate new electronic elements characterized by much better properties than conventional ones. The potential use of carbon materials in electronic systems prognosticates an emergence lightweight, thin, energy-saving, biodegradable and flexible devices; variability and variety of organic materials is huge. Due to the high absorption coefficient carbon nanomaterials can be used in optoelectronics only as a of low thickness structures like thin films.

The most promising materials are carbon nanotubes (CNTs) thin films [1]. Such films present high visible light transmission, good electrical conductivity and excellent mechanical strength. For these reasons they are perfectly suitable for optoelectronic devices electrodes [2,3] or functional coatings [4,5]. CNTs thin films are especially interesting as an electrode material in organic photovoltaics—as the working [6–8] and the counter electrodes [9,10]. Ultrathin films composed of pure CNTs, their polymer composites [11,12] as well as CNTs functionalized by inorganic materials have been already studied [13–15]. A variety of methods of obtaining thin CNTs films such as spray deposition, transfer printing [16], spreading/coating [17] or dielectrophoresis [18] have been developed. However, in spite of many advantages of such methods Langmuir technique (deposition from water–air interface) provides the most controllable process of creating CNTs thin films [19].

In Langmuir technique material is formed as monolayer floating on the water–air interface and then transferred on substrate emerged or immersed in subphase. Therefore, it is possible to transfer a material layer by layer controlling the thickness of the coating with an accuracy of the monolayer thickness. Langmuir technique of CNT film creation was used for the first time by Kristic et al. [20]. However, the main problems of that method are: (1) CNTs aggregate formation on the water–air interface and (2) receiving a homogeneous layer of sufficient large area. Functionalization of CNTs helps to avoid the first point and allows to achieve well oriented CNTs layers [17,18,21,22] but obtaining a ultrathin, homogeneous and large area CNTs coating still remains unachievable.

Abbreviations: CNTs, carbon nanotubes; MWCNTs, multiwall carbon nanotubes; L, Langmuir; LS, Langmuir–Schaefer; PVC, polyvinyl chloride; LSM, confocal laser scanning microscope; SEM, scanning electron microscope; UV–vis, ultraviolet–visible; IR, infrared; PAS, photoacoustic spectrum.

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Thus, in this work we present a modified Langmuir technique newly established by us for producing a large area of homogeneous, transparent and conductive monolayers of multiwall carbon nanotubes (MWCNTs). Aggregation of a material is avoided without functionalization of MWCNTs with the use of the proposed method. The obtained CNTs monolayer is transferred onto a solid substrate and characterized by relatively high light transmission and high electric conductivity. In the paper we present the experimental results and discuss the nanometric properties of MWCNTs in a form of the Langmuir monolayers on hydrous interface and their Langmuir–Schaefer (LS) layer on a quartz plate and flexible polyvinyl chloride (PVC) foil.

The aim of this study is to establish prognostic feature of CNTs as new optoelectronic materials for their applications in modern electronics in the nearest future.

2. Materials and methods

Multiwall carbon nanotubes (Sigma-Aldrich) in powder and in a form of Langmuir monolayers and Langmuir–Schaeffer layers were used in our experiments. Their geometrical parameters were: the diameter ranges from 110 to 170 nm and length 5–9 μm. The samples were dissolved in spectrally pure dichloroethane (DCE) (Sigma-Aldrich). In this solvent the nanotubes were in a form of very stable suspension. Moreover, DCE is highly volatile and relatively low dense; it means its features fulfilled requirements for the Langmuir (L) and Langmuir–Schaefer (LS) techniques [23]. The samples were prepared as follow: 10 mg of MWCNTs was added to 30 ml DCE and then the samples undergo sonication (Ultrasonic Bath–POLSONIC; 300 W) for 30 min. Then, the suspension was being kept in a glass container for 48 h to let heaviest fraction of the suspension to go down. Next, 25 ml of the top part of sample suspension was collected and 25 ml DCE was added and sonicated again for 15 min. MWCNTs suspension was very stable—after 30 days at about 4 °C no sediment was observed.

Ultrathin layers of investigated MWCNTs was obtained on the water–air interface (L layer) and then transferred on the substrate by horizontal lifting (LS layer). The L carbon layer was created with a KSV 2000 minitrough (KSV Instruments Ltd.). Temperature of subphase was achieved and kept constant (21 °C) with a cooling circulator. Deionized water (electric resistivity 18.2 MΩ cm) obtained with a Milli-Q water purification system (Millipore Corp.) was used as the subphase. MWCNTs suspension dissolved in DCE was spread carefully onto the subphase and DCE was evaporated. The floating film was compressed symmetrically from both sides with motion barrier speed of 5 mm/min (rate of surface compression: 750 mm^2/min). In the next step of the experiment the MWCNTs monolayers were transferred on a solid plate (quartz and PVC film) taking advantage from the Langmuir–Schaefer method with the use of a KSV system (KSV Ltd.) equipped with a homemade Teflon trough of dimensions 695 mm × 75 mm (52125 mm^2). The MWCNT layers were deposited on a quartz plate (25 × 30 mm) or polymeric foil (PVC) of 0.15 mm thickness and of various sizes up to 60 × 40 mm. The quartz plate was cleaned with RCA-1 method whereas the PVC film with the use of the ultrasonic bath fulfilled up with isopropyl alcohol. The all solid surfaces were repeatedly rinsed up with Milli-Q water before transferring MWCNTs nanotubes.

The standard method of obtaining L layer [24] applied to create monolayers of investigated MWCNTs was extremely ineffective—the layers were inhomogeneous and the results were non-repeatable. Thus we decide to prepare the L layers with the use of an improved Langmuir method and then transferring material on solid substrate by a standard LS method (lifting a horizontal oriented substrate) in the similar way as it was done and described in [25]. Fig. 1 shows the detailed scheme of the modification

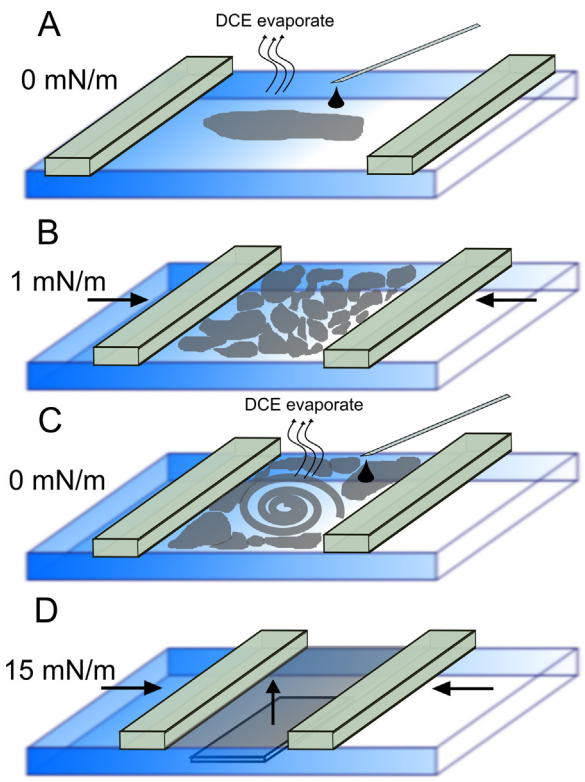

Fig. 1. Schema of Langmuir technique modifications; precise description in text.

procedure. The homogeneous layer was done in a few steps as follows: (i) MWCNTs suspension was spread drop by drop on the water subphase and after 30 min solvent was evaporated (Fig. 1A), (ii) a layer was compressed up to the surface pressure not higher than 1 mN/m (Fig. 1B) and in contrast to the standard Langmuir method, compression was stopped, (iii) extra 10% of suspension was spread drop by drop (Fig. 1C); during spreading the surface pressure did not excess 3 mN/m to avoid some unrecoverable changes in the layer. The decreasing surface pressure was observed after 30 min and it dropped to 0 mN/m, (iv) in the last stage the modified L layer was being compressed to the required pressure (5, 15 and 25 mN/m) and then was horizontally lifted onto a solid substrate (Fig. 1D). A comparison of the images of the layers created with the use of the two methods let to discuss how the extra suspension affected the layer (Fig. 1C) (step (iii)). After solvent evaporation the small islands of MWCNTs at the air–water interface with the densely packed material were formed and they were separated by uncovered "spots". During surface pressure increasing the islands pressed one to another preventing to fill the entire layer. In the modified L method the compression was stopped at 1 mN/m—e.g. when the MWCNTs islands were not fully aggregated. When droplets of extra suspension fell on the interface the islands were broken. Moreover, evaporating solvent (DCE) caused mixing of the material. Because the area of layer was limited by the barriers (step (ii)) material has no sufficient room to create aggregates as small islands and thus it formed a homogeneous L layer. After transferring layer on the solid substrate a densely packed nanolayer of MWCNTs in the large area was obtained as described above.

A laser scanning confocal microscope (LSM) (LSM710 Zeiss) in the material mode was used for characterization of the layers on solid substrates. A 458 nm laser beam was used in the experiment. Moreover, a scanning electron microscope (SEM) (FEI NOVA NANOSEM 650) under voltage from 1 to 30 kV was also used for layer characterization. The carbon nanotubes layer on PVC was