Journal of Physics and Chemistry of Solids 93 (2016) 68–72

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

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

Technical note

Piezoelectric properties of diphenylalanine microtubes prepared from the solution

Semen Vasilev [a], Pavel Zelenovskiy [a], Daria Vasileva [a], Alla Nuraeva [a], Vladimir Ya. Shur [a], Andrei L. Kholkin [a,b,*]

[a] Institute of Natural Sciences, Ural Federal University, 51 Lenin Avenue, 620000 Ekaterinburg, Russia
[b] Physics Department & CICECO – Materials Institute of Aveiro, University of Aveiro, 3810 – 193 Aveiro, Portugal

ARTICLE INFO

Article history:
Received 20 November 2015
Received in revised form
21 January 2016
Accepted 6 February 2016
Available online 11 February 2016

Keywords:
Diphenylalanine
Microtube
Piezoelectricity
Piezoresponse force microscopy

ABSTRACT

Biomimetic self-assembling peptides form a variety of structures that can be used for the fabrication of functional devices. We are witnessing the emergence of a new era of bionanotechnology that opens up new possibilities for novel electronic, photonic and energy functionalities based on supramolecular green and lightweight structures. In this work, we study the emergent piezoelectric properties of linear dipeptide diphenylalanine (FF) that can self-assemble in the shape of microtubes. The matrix of piezoelectric coefficients is derived for the first time based on the hexagonal symmetry of FF structures and different configurations of the tubes are tested by the advanced Piezoresponse Force Microscopy (PFM). Strong piezoelectric anisotropy of piezoelectric coefficients is explained by the self-assembled structure of FF peptides. Possible applications of piezoelectric microtubes in functional devices are discussed.

1. Introduction

Self-assembly of biomimetic functional materials is a convenient tool for the fabrication of functional nano- and micro-devices with emerging properties [1]. Peptides are in particular important as molecular building blocks because of their flexibility and variability in molecular design [2]. Self-assembling peptides possess unique characteristics that can be tuned by changing the amino acid sequence and conjugating chemical groups to reach better functionality [2,3]. Their assembly mechanisms are determined by noncovalent intermolecular interactions such as electrostatic, hydrophobic, Van der Waals, hydrogen bonds, and aromatic π-stacking [4]. They can readily adopt diverse 3D architectures such as vesicles, micelles, monolayers, bilayers, fibers, tubes, ribbons, and tapes [5]. In particular, diphenylalanine (L-Phe-L-Phe, FF) self-assembled nanotubes demonstrate various outstanding physical and chemical properties, which are interesting both from the fundamental and applied points of view [6–8]. Chemical and thermal stabilities of this material allow using it for the novel design of biosensors, bioelectronics, and biomolecular devices [9], whereas its strong piezoelectricity makes it an advanced functional material for the development of biocompatible nanoscale piezodevices [10,11]. Piezoelectric properties of FF nanotubes have been previously evaluated using shear piezoelectric effect (i.e. changing the angles in the unit cell under the application of electric field normal to polarization direction) [10]. The measurement has been done by the Piezoresponse Force Microscopy (PFM) that allows accurate measurements of the local displacements under an applied electric field. In this way, local piezoelectric coefficients can be determined provided the electric field penetration length is less than the wall thickness [12,13]. Later, strong piezoelectric properties of dipeptides have been confirmed by the observation of sharp piezoelectric resonances (both longitudinal and bending) [14], thus pondering their applications in bioMEMS and other biology-related applications. However, for the comprehensive use of nano- and microstructured peptides in piezoelectric applications, an entire set of the piezoelectric coefficients is needed. For hexagonal symmetry of FF dipeptides (space group $P6_1$), there are four independent piezocoefficients: d_{33}, d_{31}, d_{15}, and d_{14} [15]. In this work, their measurement was attempted on sufficiently big microtubes grown by crystallization from the solution. The results confirm earlier investigations and show a great potential of using FF peptides in piezoelectric applications.

2. Experimental procedure

We used FF powder purchased from Bachem, Switzerland. The powder was dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) to prepare a solution with FF concentration 100 g/L. After that, 2 μL

* Corresponding author at: Institute of Natural Sciences, Ural Federal University, 51 Lenin Avenue, 620000 Ekaterinburg, Russia.
E-mail address: kholkin@ua.pt (A.L. Kholkin).

http://dx.doi.org/10.1016/j.jpcs.2016.02.002
0022-3697/

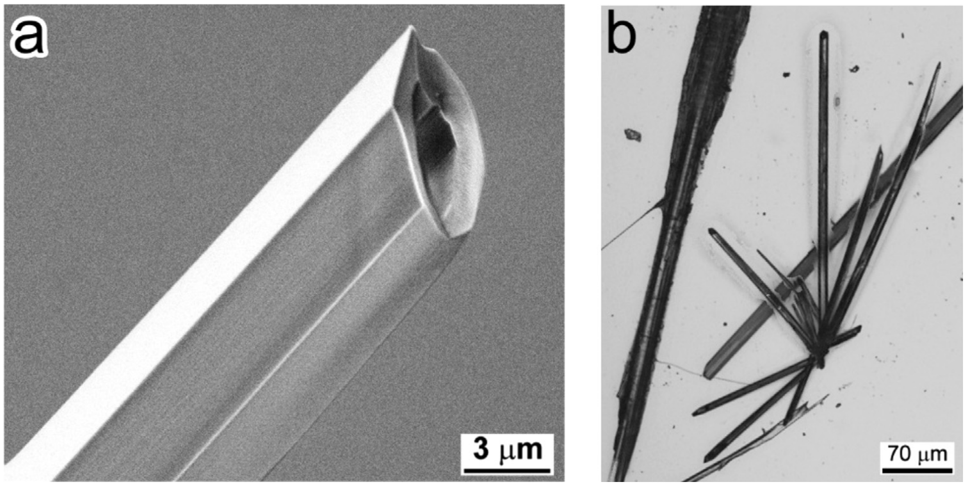

Fig. 1. (a) SEM image of peptide microtube, (b) Optical image of vertical microtubes.

of obtained solution was put on Pt/SiO/Si substrate, which was previously cleaned in acetone by lint-free cloth. Then, 98 μL of deionized water was added in order to make concentration of FF in solution equal 2 g/L. The droplet was dried at ambient conditions (22 °C) in open air. The solution was left to dry naturally, so that sufficiently big microtubes could be grown making use of the Marangoni effect in microdroplets [16]. The details of the preparation procedure are described elsewhere [17].

Optical images were obtained by optical microscope Olympus BX-51 (Olympus, Japan) in reflection mode. Objective 5 × was used for optical images capturing. Images of vertical tubes were obtained by method of layering multiple images with different focal lengths because of significant height of the tubes (Fig. 1b).

High resolution investigation of microtubes was performed by Scanning Electron Microscopy (SEM) in a secondary electron mode using AURIGA CrossBeam workstation (Carl Zeiss, Germany). For SEM investigation, the samples were covered with 6 nm of Cr by magnetron-sputtering system (Q150T, Quorum Technologies, UK). SEM image of the representative microtube is shown in Fig. 1a.

The tubes were characterized by the X-ray diffraction and Raman spectroscopy methods (see Supplementary Information section). The measurements proved that the microtubes are well crystallized and their structure is identical to that firstly described by Gorbitz [18].

To characterize the piezoelectric properties via PFM, we used commercial Atomic Force Microscopes (AFM) Asylum MFP-3D (Asylum Research, Oxford Instruments, UK) and Ntegra Aura (NT-MDT, Russia). PFM images of peptide microtubes were acquired by applying a range of ac voltage (0.1–10 V, peak-to-peak) with frequency of 20 kHz. Conductive probes (stiffness 3–5 N/m, resonance frequency 45–70 kHz) were used for the PFM measurements at ambient conditions. The cantilever response due to electromechanical coupling was detected using internal lock-ins of the AFM.

Piezoelectric coefficients of the microtubes were measured in three different configurations (Fig. 2). In the first configuration (Fig. 1a), individual tubes with the lengths of 700–1000 μm and diameters of 20–30 μm were measured on the same substrate on which they were grown. The lateral PFM signal (LF) was acquired in this case, which is proportional to the shear piezocoefficient d_{15}. Another substrate was used for measuring d_{31} and clamped $(d_{33})_{clamp}$ piezoelectric coefficients. The substrate had split metal electrodes (width about 400 μm, height about 30 μm); the tubes were manually attached to electrodes by silver paste. The measurements were done in the central part of tube in between the electrodes (Fig. 2b). The voltage was applied between the electrodes and displacements were measured either in the vertical direction (DFL signal) to yield d_{31} coefficient or in the lateral mode (LF signal) to acquire $(d_{33})_{clamp}$. In this case, the cantilever was just used as a displacement probe. In the third configuration, vertical tubes were measured that were electrically aligned by the electrostatic effect.

The values of all piezoelectric coefficients (except of d_{33}) were determined in the following way. The PFM scans ($0.5 \times 1.5\ \mu m^2$) were performed under increasing ac voltage. Then the piezoresponse value was averaged on the entire scan and the displacements were plotted as a function of the voltage (Fig. 3). The respective piezocoefficient was determined by the slope of the

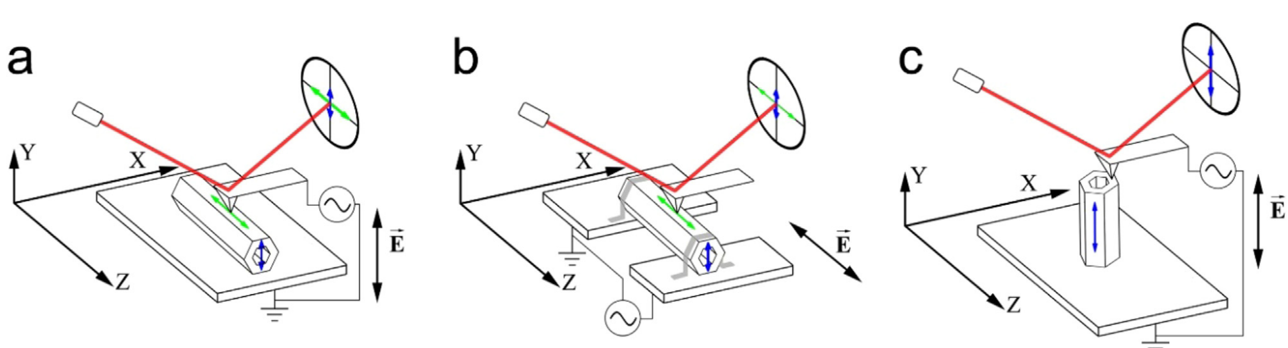

Fig. 2. Schematics of different configurations for the measurements of piezoelectric coefficients. (a) Measurement of d_{15} (LF signal, displacements are shown by horizontal arrow) and d_{14} (DFL signal, vertical arrow). (b) Measurement of $(d_{33})_{clamp}$ (LF signal,horizontal arrow) and d_{31} (DFL signal, vertical arrow). Tube was fixed by conductive glue (silver paste). (c) Measurement of d_{33} (DFL signal,vertical arrow). Red line shows the laser beam reflecting from the cantilever. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)