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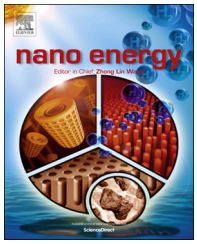

RAPID COMMUNICATION

Epitaxial growth of vertically aligned piezoelectric diphenylalanine peptide microrods with uniform polarization

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Abstract
Energy harvesting with piezoelectric nanomaterials spurred the development of self-powered nanosystems, and piezoelectric biomaterials are expected to play an important role in the biomedical field. Bio-inspired piezoelectric diphenylalanine (FF) peptide microstructures were fabricated on various substrates through a novel epitaxial growth approach. The low-temperature process produced vertically aligned FF peptide microrods with hexagonally arranged nanochannels and uniform polarization. Direct measurement of the piezoelectricity was achieved for the first time from a solid FF peptide single crystal and yielded an effective piezoelectric coefficient d_{33} at 9.9 pm/V. The dense and aligned FF peptide microrods are advantageous for energy and sensing applications.

Introduction

Molecular self-assembly of bio-inspired materials has attracted much research effort in recent years due to its potential to fabricate novel bottom-up structures for new applications. Among them diphenylalanine (FF) peptide, which is highly biocompatible with low to no cytotoxicity [1-3], has been widely explored recently as a potential candidate for various applications such as supercapacitors [4-6], electromechanical sensing and actuation [7], optics [8,9], nanostructure fabrication [10], and drug delivery [2]. Many of those applications aim to take advantage of the hydrophilic nanochannels and charge polarization which are inherent in the crystal self-assembled by linear FF molecules [11,12]. Strong piezoelectricity has been demonstrated in FF peptide nanotubes. A high effective piezoelectric coefficient d_{15} at 60 pm/V was measured from the shear response of FF peptide hollow tubes [13] and d_{33} was estimated in the range of 5-50 pm/V [13-15]. However, the current long and slender micro/nano tubular structures lacking in large-scale alignment may prevent effective access to the nanochannels. In addition, the coercive field was estimated on the order of ~30 MV/cm which made polarization switching practically impossible [15]. The current FF peptide nanotubes show random polarizations from the

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growth. The growth of FF peptide nano and microstructures with uniform polarization is needed in order to observe and take advantage of the piezoelectricity at large-scale.

Here we report a new and scalable approach to the controlled fabrication on various substrates of vertically aligned FF peptide microrods with uniform polarization. We start by engineering a textured seed layer with preferential vertical orientation, and then grow the FF peptide microrods epitaxially from this seed layer. Unlike high temperature processes which yield cyclic-FF structure without nanochannels and charge polarization [16-18], our simple process is mostly done at room-temperature and the produced linear-FF peptide is of hexagonal crystal structure with nanochannels and spontaneous polarization. This novel approach provides for good alignment of the material in cases where it will be used for structural applications. In applications where large-scale, uniform piezoelectricity of the material is required, this can be achieved by the application of an electric field during growth. This polarization under electric field is independent of the good structural alignment achieved by our method. Characterization techniques such as X-ray Diffraction (XRD) and Piezoresponse Force Microscopy (PFM) consistently suggest that the hexagonal crystal structure is maintained. The measured effective piezoelectric coefficient d_{33} of the FF peptide microrods is comparable to that of ZnO nanowires [19]. Our work can enable new applications of bio-inspired materials in areas such as energy harvesting and storage, electromechanical sensing and actuation, drug delivery, as well as fundamental studies of FF-based structures.

Experimental

Preparation of seed layer

Diphenylalanine lyophilized powder H-Phe-Phe-OH (FF) was purchased from Bachem and stored in an enclosed dry container at 0 °C. 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) was purchased from Sigma Aldrich and stored in a dry container under ambient conditions. The schematic of the fabrication process is shown in Figure 1a-c. First, the FF stock solution was prepared by dissolving lyophilized FF powder in HFP to a concentration of 50 mg/mL in a glove box (water content < 1000 ppm) to minimize water absorption to the source materials. 25 μL of the stock solution was then dropped on a substrate placed in a desiccator. The drop was quickly vaporized as the desiccator was pumped down to 200 Torr in 10 seconds and then vented with compressed dry air (water content < 6 ppm). A transparent amorphous film was formed on the substrate after the evaporation completed, Figure 1a. The low water vapor content in the growth environment with relative humidity (RH) lower than 50% is essential to prevent unintentional crystallization of the amorphous film [20]. This amorphous film was then transferred to an enclosed box which was connected in a closed loop of flowing moist air with RH ~100% (Figure 1b). The amorphous film was intentionally crystallized into a seed layer by vigorously circulating the humid air through the enclosed box for 90 s.

Epitaxial growth of FF peptide microrods

The epitaxial growth from the seed layer was achieved by the precipitation of a saturated FF aqueous solution, Figure 1c. First a concentrated FF aqueous solution was prepared by mixing 75 mg FF with 50 mL deionized (DI) water and kept in an oven at 65 °C until the FF powder was fully dissolved. The substrate with the prepared seed layer was placed floating upside down on the surface of concentrated FF solution right after the solution was taken from the oven. Ventilation from a small fan was used to facilitate cooling and evaporation of water in the concentrated FF solution. Most of the water had evaporated after about 6 h. The substrate with FF peptide microrods was then taken out, briefly cleaned with DI water, and dried with compressed air. The growth process is not limited by the

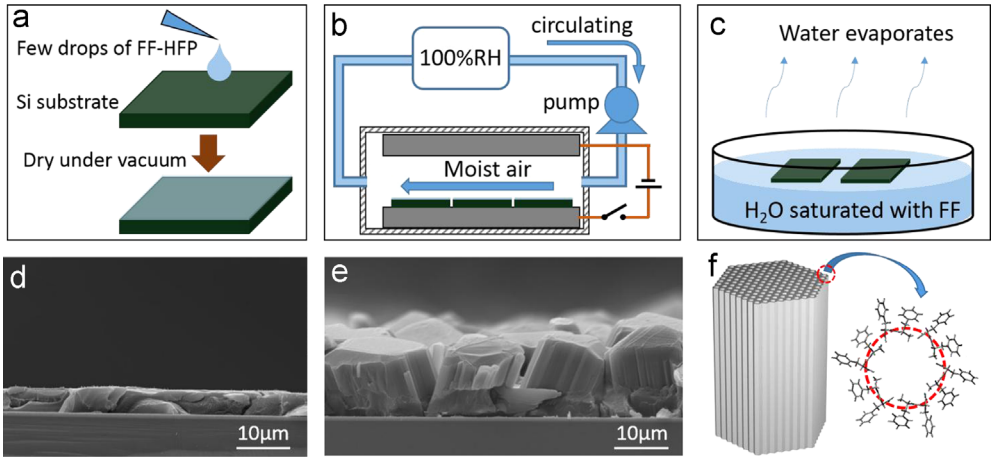

Figure 1 Schematic illustration of the fabrication process (a-c) and SEM images and model of FF peptide microrods (d, f). (a) Formation of an amorphous FF peptide layer on the substrate. (b) Formation of the FF peptide seed layer through the crystallization of the amorphous layer from (a). (c) Self-assembly of FF peptide molecules for epitaxial growth of FF peptide microrods. Side SEM image of the seed layer (d) and FF peptide microrods grown in the absence of electric field. (f) Illustration of FF peptide microrods with hexagonally arranged nanochannels. The enlarged circle illustrates a nanochannel enclosed by six FF peptide molecules.