Controlled growth of aligned α-helical-polypeptide brushes for tunable electrical conductivity

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(Received 15 December 2010; accepted 5 February 2011; published online 30 March 2011)

Polypeptide based molecular diode with high rectification ratio (~122 at ±0.422 V) is formed by controlling molecular order and orientation. A film of tethered poly(γ-benzyl-L-glutamate) (PBLG) with high degree of molecular orientation was formed by solvent pair (good/bad) treatment. I-V characterization of the well aligned polypeptides showed that the rectification ratio of PBLG was sufficiently large for potential diode and transistor applications. © 2011 American Institute of Physics. [doi:10.1063/1.3560452]

The electronic properties of polypeptides have drawn significant interest because the electron transport process of biological molecules is controllable and highly efficient, and largely relies on modulation by peptides.2 It is known that peptides with α-helical structures possess a large dipole moment created by the sum of the small dipoles of amino acid repeats.3,4 Electrical studies on peptide monolayer have examined the effects of dipole direction,5–7 linkers,8,9 chain length,10 and side chains.11 These studies have confirmed electron transfer through the α-helical peptide monolayer, with the most efficient transfer occurring in the direction from the C- to N- terminus of the molecular axis, which coincides with the internal electric field generated by the α-helical dipole.8,11–14 The asymmetric I-V curves of peptide monolayers were obtained, with their rectification ratio (RR) of ~10 (RR is defined as the absolute value of the ratio of the currents I at bias V and −V, respectively; i.e., RR(V) = |I(V)/I(−V)|).15,16 In these studies, peptide films consisted of short, tethered, randomly oriented peptide chains (~10–30 amino acid units). The random orientation, which occurred despite the end-terminating to the substrate, was likely caused in part by the mutual repellation of intermolecular dipoles; the average helical tilt angles measured in the end-tethered peptide monolayer films were ~25°–65° from the surface normal. As motivated by the previous examples of organic electronic materials, where conducting polymer nanotubes,17 nanowires,18 and nanorods19 showed higher conductivity with an anisotropic order than those with the isotropic state, we anticipated that the orientation and morphology of biological materials could also play a critical role on the electrical properties.

Here we present a method for designing and controlling the collective molecular orientation and organization of polypeptide films. We used surface-initiated vapor deposition polymerization of the N-carboxyl anhydride of benzyl-L-glutamate on a surface bound amine initiator to fabricate films of end-tethered poly(γ-benzyl L-glutamate) brush (t-PBLG) shown in Fig. 1(a).20 Previously we have demonstrated that treatment of such t-PBLG films with sequential exposure to good and bad solvents, the “solvent quench” approach, assembled the α-helical t-PBLG chains into nearly perpendicular molecular bundles.21 The combination of two techniques produced chemically stable t-PBLG monolayers with film thicknesses ranging from a few to hundreds of nanometers,22 suitable for many electronic and optoelectronic applications.

To study the effect of t-PBLG orientation on its electrical behavior, we prepared t-PBLG samples on Au-coated Si (100) wafers (sample size: 6 cm²), with and without subsequent solvent quenching (designated as Qt-PBLG and UQt-PBLG, respectively). A 100-nm-thick, spin-coated PBLG film (SCPBLG) was also prepared as a control. The atomic force microscopic (AFM) image [Fig. 2(a)] showed that the SCPBLG on Au had no apparent nanostructure, and had an average surface roughness (Rₚ) of 0.9 nm (based on an AFM image size of 1.25 μm × 1.25 μm). AFM and scanning electron microscope (SEM) studies revealed that a 40-nm-
thick, dense, granular UQt-PBLG film was converted into a collection of upright, 110-nm-tall PBLG bundles in the Qt-PBLG sample by solvent quenching. For the t-PBLG brush samples, the UQt-PBLG film was composed of ∼5 nm granules [Fig. 2(b)], with $R_a = 4.2$ nm, and the Qt-PBLG film consisted of upright, conelike bundles [Fig. 2(c)] with $R_a = 36$ nm. The contrast in structure of the three films and the film thickness were also apparent in both plane-view and cross-sectional SEM images, in which the SC$_{PBLG}$ film appeared homogeneous, while the 40-nm-thick UQt-PBLG film had a granular structure, and the Qt-PBLG film was composed of a collection of ∼110-nm-tall, intertwined, vertically oriented bundles [Figs. 2(d)–2(i)].

The difference in molecular order in the Qt$_{PBLG}$- and UQt$_{PBLG}$ films was further analyzed by comparing the average helical tilt angles of the PBLG chains in the two samples. The average helical tilt angles can be calculated from the ratios of the absorbances of the amide I and amide II bands for each sample based on external-reflectance Fourier transform infrared spectrometry (ER-FTIR) [see Fig. (S1), Ref. 25, and calculation of tilt angle of PBLG by ER-FTIR in Supplemental Information]. The average rotational tilt angles from the surface normal were 75°, 57°, and 13° for the SC$_{PBLG}$, UQt$_{PBLG}$, and Qt$_{PBLG}$ films, respectively. Based on the AFM, SEM, and ER-FTIR, as well as previous electro-optical studies of PBLG films, we concluded that the PBLG molecular chains in SC$_{PBLG}$ film were randomly dispersed and lying flat, whereas the UQt$_{PBLG}$ had more order and a greater chain orientation and Qt$_{PBLG}$ had the best molecular order perpendicular to the surface [Figs. 1(c)–1(e)].

Conductive-AFM (C-AFM) was utilized to examine the electrical properties of the SC$_{PBLG}$, UQt$_{PBLG}$, and Qt$_{PBLG}$ samples at ambient conditions. The current-voltage (I-V) curves were measured at the locations shown by point A in the respective AFM images [Figs. 2(a)–2(c)]. The direction of positive bias and current were defined as going from the top electrode [C-AFM tip (Cr/Pt coated cantilever)] to the Au-coated substrate. As shown in Fig. 3, the differences in the electrical behavior of the three PBLG samples were clearly correlated with their molecular organization. The SC$_{PBLG}$ film, which completely lacked molecular order, exhibited insulatorlike behavior with the current fluctuating around 0.1–10 pA [Fig. 3(b)]. In contrast, the tethering of individual PBLG chains on the surfaces might have prevented them from forming completely antiparallel pairs, such that a net dipole moment in the perpendicular direction existed in both t-PBLG films. The UQt$_{PBLG}$ film exhibited an asymmetric I-V curve with the current increasing more with the positive bias than with the negative bias. The maximal RR was ∼13, which is on the order of previously reported peptide monolayers and molecular diodes. For the Qt$_{PBLG}$ film, it consisted of the most aligned, periodic molecular bundles, demonstrating the highest RR of the three samples. Based on the SEM side view image, the molecular chain at the center of the bundle in the Qt$_{PBLG}$ film was ∼110 nm in length, corresponding to ∼730 amino acid repeats (0.15 nm/residue along the molecular axis), resulting in an unprecedented, huge dipole moment of ∼2550 D (3.5 D/residue) along the surface normal. As a result, the electron transport efficiency was highly enhanced. As shown in Fig. 3, the Qt$_{PBLG}$ sample showed unambiguous diode characteristics, coinciding with the direction of the oriented α-helical dipole. The current was increased exponentially in the forward biased region, and quickly reached the instrumental limit of 0.5 A. On the contrary, there was small reverse saturation current in the corresponding reverse biased region. As a result, we obtained the RR = 122 at $V = \pm 0.422$ V. It is reasonable to attribute the electric behavioral differences to the differences in the net dipole moment and the net molecular orientations in the films.

To learn more about the correlation between the surface nanostructure and the electrical behavior of the films, the I-V curves of the Qt$_{PBLG}$ film were measured by C-AFM at a number of locations A to E [Fig. 4(a)]. This cross-sectional profile is referred to the white line on Fig. 2(a). As shown in Fig. 4(b), at the top of the bundle (point A), the I-V curve was the most asymmetric of any of the measurement locations and had the largest RR value, RR$_{A} = 122$. At the shoulders of bundles, slightly lower RR values were measured, with RR$_{B} = 9$ for point B, and RR$_{C} = 13$ at point D. Similarly, at the minor vale of the bundle, the RR$_{D} = 12$ at point C. At the base (point E), the I-V
curve was linear, with high current at low bias, suggesting direct contact of the two electrodes.

The morphological dependence of the rectification ability of the QxPBLG film offered further confirmation of the effect of chain orientation on the electrical properties of the PBLG films. It is likely that at point A, where the molecules in the center of the cone are well-aligned, one might have a better chance of detecting the electric current at or near the tip of the α-helical chain, which would provide the most highly enhanced rectification. At the shoulder of the bundle, however, the C-AFM was probably in contact with shorter PBLG chains or the midsection of PBLG chains, resulting in decreased values of RR.

In the C-AFM study of the QxPBLG film, the current reached the detection limit of C-AFM when the positive bias exceeded 0.422 V. Both $dI/dV$ and $d^2I/dV^2$ reached the detection limit of C-AFM when the positive bias was already high. $dI/dV$ was at least 106 times higher than that of a spin coated PBLG tip of the same film composition but different orientation in films, the electrical anisotropy of the Qt-PBLG film offered further confirmation of the morphological dependence of the rectification ability of the Qt-PBLG film. The result suggests that the RR value could conceivably be large if we could measure the current at voltage higher than 0.422 V. Nevertheless, even a current of 0.49 μA at 0.422 V was already high (the current density through a single molecular bundle was $\sim 2.5 \times 10^4$ A/cm² by assuming tip-bundle contact area of 2000 nm², as the tip radius is 25 nm). We further estimate larger area current density $\sim 10^5$ A/cm² by assuming that there were approximately 20 molecular bundles/μm². The estimated current density was at least 10⁶ times higher than that of a spin coated PBLG film (SCPBLG), and was of the same order of magnitude, if not higher, than that of regular organic thin film diodes.

Our data suggested that the electron transport in the PBLG film is highly anisotropic, and strongly correlated with the helical and dipole order. This observation may be supported by the recent ab initio calculations, which predicted that the α-helical peptide backbones possess intrinsic diode characteristics, and that the electrons transport through the hydrogen bonds along the helical axis. Other explanations include the well-aligned helices serving as electron tunnels, or electrons hopping through the well-aligned benzyl side chains, in the direction of net dipole.

In conclusion, we have shown that the collective electrical property of the polypeptide brushes highly depends on the net molecular dipole order. With an identical chemical composition but different orientation in films, the electrical characteristic was varied from insulator to diode. Specifically, the oriented bundles of PBLG helices exhibited highly enhanced RRs, with a magnitude that is comparable to that of current, state-of-the-art organic diodes. The large RR, as well as the appreciable conductivity of the quenched t-PBLG films, combined with their ease of synthesis, should make these biomaterials viable candidates for use in molecular photodiodes, transistors, signal rectifiers, radio frequency identification tags, and flexible displays.

This work was supported by the grants from Academia Sinica and National Scientific Council, Taiwan (Contract Nos. 94-2120-M-003-001, 95-2120-M-003-002, and 96-2120-M-003-003 to Ying-Chih Chang). We thank Professor Dr. Winston Chen, Professor Dr. Yuan Lee, Professor Dr. Yu-Ling Wang, and Professor Dr. Chun Wei Chen for the discussion, and Mr. Hung-Chun Lo, Mr. Che-Yu Kuo, and Mr. Chih-Jung Hsu for experimental assistance.