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Review

Proteins as functional interlayer in organic field-effect transistor

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ABSTRACT

The paper summarizes and discusses the recent advances of proteins as functional interlayers in organic field-effect transistors (OFETs). Specific focus is given on the proteins integrated into the device structure, either to act as dielectric materials or to perform as the functional interlayer between the dielectric and the organic semiconductor (OSC). The main emphasis is give to the location and the specific effect of protein layers in the structure of OFETs. Besides, the possibility of amyloid serving as useful building blocks for OFET is discussed.

1. Introduction

Organic field-effect transistors (OFETs) have gained great attention over the last years because of their potential applications in low-cost, flexible, and large-area electronic products, such as digital displays, electronic paper, radio frequency identification tags, and label-free sensors [1–3].

Due to their unique merits such as bioadhension, biocompatibility, biodegradability and no need for chemical synthesis, natural biological materials, namely, DNA [4], carbohydrates [5], peptides and proteins [6,7] etc, have been extensively integrated in OFETs devices fabrication as gate substrate, dielectrics and organic semiconductor (OSC). If used properly, these natural materials can actually simplify the OFET fabrication process, reduce the costs, and enhance the performance of the devices. So, the incorporation of natural biological materials in OFETs unfolds new perspectives for the exploitation of biosystems and holds much promise in bioelectronics application [8].

In this mini-review, we summarize and discuss the recent advances of proteins as functional interlayers in OFETs. This review is mainly restricted to the discussion of back-gate OFETs which are made from a gate electrode, a dielectric layer, an OSC, a source and a drain electrode from bottom to top in turn. Specific focus is given on the proteins integrated into the device structure, either to act as dielectric materials or to perform as the functional interlayer between the dielectric and the OSC. At last, the possibility of amyloid, a special type of protein structures with multiple excellent properties, serving as useful building blocks for OFET is also discussed.

2. Proteins as dielectric layers

Among the structural layers in OFET architectures, proteins can serve as dielectric layers for the majority of naturally occurring proteins have insulating properties. Furthermore, proteins are biodegradable and often have unique properties that cannot be easily achieved by conventional organic or inorganic insulating materials. In the subsequent sections, the development of OFETs based on protein dielectrics is discussed. Among the most used proteins employed directly as dielectrics are silk fibroin, bovine serum albumin (BSA), collagen, and gelatin. Special attention is paid to the significant enhancement of electric properties of the devices. Meanwhile, the remaining challenges are also outlined.

2.1. Silk fibroin

Silk fibroin (SF) is one of the silk proteins spun by silkworms. It is a natural biopolymer consisting of the repeated amino acids of glycine (Gly) and alanine (Ala) in alternating sequence. The structure consists of extended polypeptide chains bonded together

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by lateral N—H···O hydrogen bonds to form antiparallel-chain pleated sheets [9]. The merits of SF, such as low cost, lightweight, and large area, make it promising potential for a wide variety of applications in organic electronic devices. To the best of our knowledge, SF was the first and one of the most reported proteins in OFETs so far.

Capelli et al. [10] integrated SF into electronic and optoelectronic devices, in which SF was used as a thin film dielectric in an OFET and an organic light emitting transistor (OLET) device. The comparisons of the mobility, threshold values and on/off ratio for silk p and n–type OFETs and respective standard poly(methyl methacrylate) (PMMA) and SiO_2 devices were as shown in Table 1. The results demonstrated natural SF can be successfully used as a dielectric material for fabricating high-performance n- and p-type organic transistors and light emitting transistors.

Taking SF as the gate dielectric and a flexible poly(ethylene terephthalate) (PET) as plastic substrate, Wang et al. [11] developed a pentacene organic thin-film transistors (OTFT) with a very high field-effect mobility (μ_{FE}) value of 23.2 cm^2 V^{-1} s^{-1} in the saturation regime and a low operating voltage of −3 V. Based on the detection results by atomic force microscopy (AFM) and grazing incidence X-ray diffraction (GIXRD), the authors considered that the primary roles of the SF dielectric is to increase the pentacene orthorhombic phase and to reduce the amorphous phase in the pentacene layer prepared by thermal evaporation. In a word, the operating speed of pentacene based OTFT was greatly improved by choosing SF as the gate dielectric material.

Solution-processed OFETs with SF as gating material and poly(3-hexylthiophene) (P3HT) as the semiconducting layer has been reported by Shi et al. [12]. The distinctive characteristic of such OFETs can be represented from the following aspects: low threshold of −0.77 V, low-operating voltage (0–−3 V) and high carrier mobility of 0.21 cm^2 V^{-1} s^{-1}. The enhancement of the performance is attributed to an array of highly ordered fibers structure originated from the high content of β strands in SF dielectric, which leads to reduce the trapping sites at the semiconductor/dielectric interface.

Different from the above documents using SF as gate dielectric independently, high sensitivity OFET based NO_2 gas sensors with silk fibroin (SF) and PMMA bilayer dielectric was reported by Li et al. [13]. The results revealed that the sensing properties of the OFET with PMMA/SF bilayer dielectric was significantly enhanced compared to that with the PMMA dielectric. The authors suggested that an increased saturation current and charge mobility can be caused by the interaction between the NO_2 and a great quantity of hydroxyl groups (–OH) of serine and the amidogen of SF molecules, thus enhancing the performance of this kind of OFET.

2.2. Chicken albumen

Chicken albumen is more easily obtained, processable, and inexpensive than other biomaterials for OFET devices. Chang et al. [14] used chicken albumen without any purification as a gate dielectric in pentacene- and C_{60}-based OFETs. The schematic of the structure of an OFET fabricated with albumen dielectrics was shown in Fig. 1. According to the method presented by the authors, a high-quality albumen dielectric layer can be prepared via spin-coating and subsequent thermal treatments. The output current of these OFETs reached 1.7–5 × 10^{-6} A without obvious hysteresis and the gate leakage currents were roughly 10^{-10} A. Compared with common polymeric dielectrics, such as PMMA and polystyrene (PS) dielectrics, the output currents of the OFETs with albumen dielectrics were double those of ordinary polymer-based OFETs. At last, the authors suggested that the intrinsic properties of chicken albumen, such as the stability, aging effect, tolerance to temperature and moisture, loss factor under different frequency regime, etc., should be further investigated for the practical application of chicken albumen dielectrics.

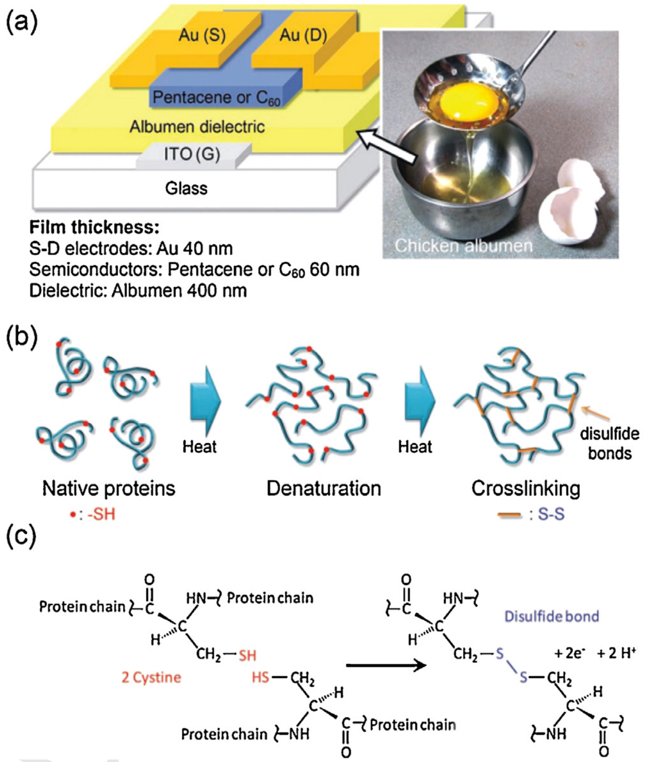

Fig. 1. (a) Sketch of the OFET structure fabricated with albumen dielectrics. (b) Schematic diagram of denaturation and the cross-linking reaction of albumen protein under heat treatments. (c) Scheme for the formation of a disulfide bond between two cysteine groups on different protein chains. Reprinted with permission from Ref. [14]. © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

2.3. Bovine serum albumin (BSA)

Bovine serum albumin (BSA) is a natural protein, in which the percent of acidic and basic amino acid residues reach ca. 34% in total [15]. So BSA is known for its good hydration ability. The effect of humidity on OFETs fabricated with BSA as gate dielectric was investigated by Lee et al. [16]. The researchers found that pentacene OFETs with BSA as the gate dielectric exhibited a field-effect mobility value ($\mu_{FE,sat}$) of 0.3 cm^2 V^{-1} s^{-1} in the saturation regime and a threshold voltage (V_{TH}) of *ca.* −16 V in vacuum, whereas, the $\mu_{FE,sat}$ value increased to 4.7 cm^2 V^{-1} s^{-1} and

Table 1
The parameters comparison of silk p and n–type OFETs with respective standard PMMA and SiO_2 devices [10].

	DH4T p-type			P13 n-type		
	Mobility (μ, cm^2 V^{-1} s^{-1})	Threshold (V_T, V)	On/off ratio	Mobility (μ, cm^2 V^{-1} s^{-1})	Threshold (V_T, V)	On/off ratio
SiO_2	4×10^{-2}	−3	10^3	1.3×10^{-1}	21	10^3
PMMA	9×10^{-2}	−20	10^2	3×10^{-1}	18	10^4
Silk	1.3×10^{-2}	−17	10^4	4×10^{-2}	2	10^4

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