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Chicken Albumen Dielectrics in Organic Field-Effect Transistors

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Biomaterials for organic electronics have gained considerable attention in recent years.[1–3] The advantages of biomaterials are that they are biodegradable, bioresorbable, biocompatible, typically environmentally friendly, and do not require chemical synthesis. Bio-organic field-effect transistors (BiOFETs) use biomaterials as semiconductors, dielectrics, and substrates. For example, β-carotene[4] has been applied as semiconductors. DNA-hexadecyltrimethylammmonium chloride (DNA-CTMA),[5–7] nucleobases,[8] and silk[9] have been used as gate dielectrics. Silk[10] and poly (L-lactide-*co*-glycolide) (PLGA)[11] have been utilized as device substrates. Biomaterials are potential candidates to simplify the fabrication process and decrease fabrication cost in organic electronics.

This work uses a biomaterial, chicken egg white, also called albumen, as a gate dielectric in pentacene- and C_{60}-based organic field-effect transistors (OFETs). The OFETs have excellent performance. The albumen was obtained directly from eggs without further extraction. Via spin-coating and thermal treatments, the albumen formed a high-quality dielectric layer on the gate electrodes and device substrates. The output currents of these OFETs with albumen dielectrics were double those of common polymeric dielectrics, such as poly(methyl methacrylate) (PMMA) and polystyrene (PS) diaelectrics. The dielectric constants of albumen, PMMA, and PS were confirmed by the capacitance–voltage (*C–V*) measurements. The surface smoothness of the albumen dielectric was similar to that of PMMA and PS dielectrics. Albumen from chicken eggs could be an ideal dielectric material for BiOFETs of a low-cost and with simple fabrication processes.

The characteristics of the albumen dielectrics for OFETs, such as electrical breakdown, hydrophobicity, and smoothness, for OFETs were strongly related to thermal baking conditions and baking sequences. Excluding water, 95% of egg white is composed of 40 different proteins with relative molecular masses of 14 800–83 000 g mol^{-1}.[12,13] Protein denaturation was mainly the unfolding of protein chains and hydrogen bond interchanges of amino acid side chains in protein molecules. Sometimes this denaturation is reversible. Irreversible denaturation of proteins, called coagulation, under thermal processes has been extensively studied.[14,15] The most important chemical reaction in irreversible thermal denaturation is the formation of disulfide bonds, also called disulfide bridges, between two cross-linked protein molecules, as illustrated in **Figure 1**b.[15,16] The disulfide bond is formed between cysteine groups, one amino acid with one thiol, on different protein molecule chains. Figure 1c shows the disulfide transformation between two cysteine groups,[17,18] 2 R–SH $\rightarrow$ RS–SR + 2 H^+ + 2 e^-. The most significant function of protein disulfide bonds in a dielectric layer of OFETs is the reduction of gate leakage current in a thermally self-crosslinking albumen film without any additional additives. We took the most advantage of the thermal crosslinking properties from natural proteins for the fabrication of organic electronic devices.

The hydrophobicity of albumen dielectrics depends on the number of hydrophobic amino acid side chains that are natively aggregated in the protein core, which is driven outward by thermal energy. An albumen film baked at 160 °C was more hydrophobic than one baked at 100 °C. The water contact angle is around 80–60° for the albumen dielectrics baked at 160 °C and of 60–40° baked at 100 °C. Additionally, the water evaporation rate during baking can affect field-effect currents of OFETs, which can alter the dielectric surface texture and smoothness. The thermal treatment of albumen dielectrics has a major influence on OFET performance. In this study, the baking process of albumen films after the spin-coating process was 100 °C for 10 min, 120 °C for 10 min, and 140 °C for 10 min to ensure the formation of a smooth and dense film for device applications.

Figure 2a–d show the output and transfer characteristics of pentacene and C_{60} OFETs with albumen dielectrics. The pentacene- and C_{60}-based OFETs had output currents of 1.7–5 × 10^{-6} A at a gate voltage V_G = –25 V and +25, threshold voltages of –8 V and +1.5, an on/off ratio of 10^4, and leakage currents of 10^{-10} A. No hysteresis existed in p-type or n-type operations. Hole and electron mobility were calculated in the saturation region[19] to be 0.09 and 0.13 cm^2 V^{-1} s^{-1}, respectively. Based on the performance of these OFETs, albumen is an excellent dielectric in both pentacene and C_{60} OFETs.

Hysteresis in BiOFETs is a significant concern in device applications and is often resolved by using the crosslinking approaches.[5–7] In our studies, hysteresis was not detected in either pentacene or C_{60} OFETs (Figure 2b,d). These results are attributed to natural protein properties, hydrogen-bond interchanges, and disulfide-bond crosslinking in irreversible thermal denaturation without any additional crosslinking agents.

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COMMUNICATION

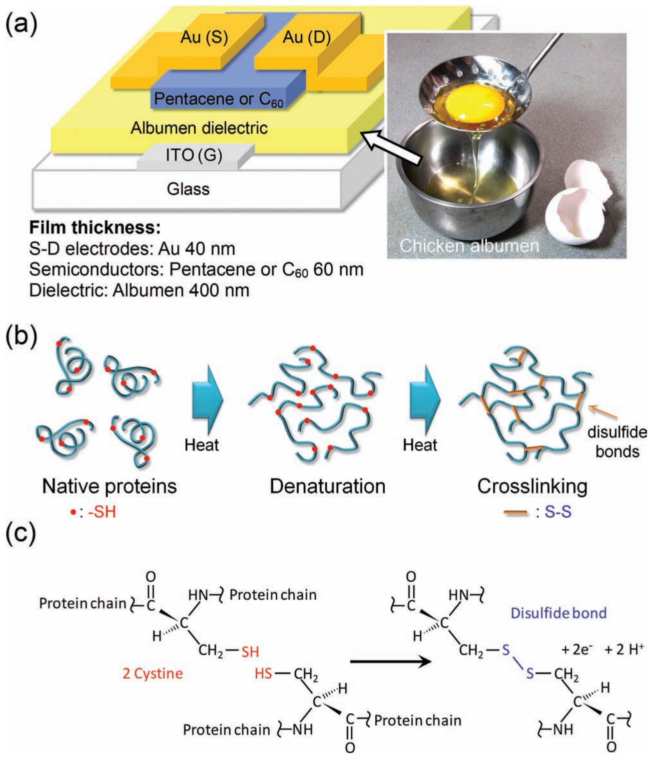

Figure 1. a) The structure of an OFET fabricated with albumen dielectrics. The right photograph illustrates the separation of egg white and egg yolk. b) The schematic drawing shows the denaturation of albumen protein and the crosslinking reaction under the thermal treatments. c) Scheme for the formation of a disulfide bond between two cysteine groups on different protein chains.

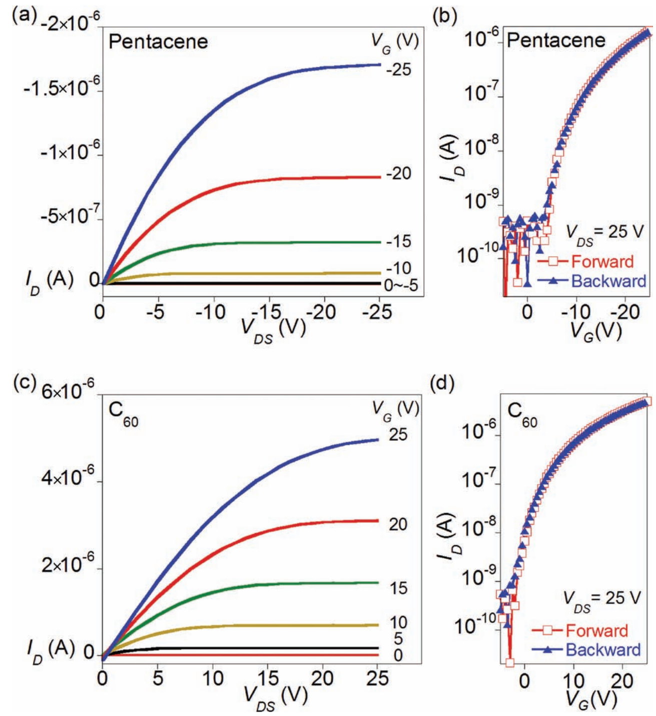

Figure 2. The performance of OFETs with albumen dielectrics. a) The output characteristics of drain-source current versus drain-source voltage (I_{DS} vs. V_{DS}) plot of a pentacene based OFET. b) The transfer characteristics of drain-source current versus gate voltage (I_{DS} vs. V_G) plot of a pentacene-based OFET under the forward and backward bias direction. c) The output characteristics of a C_{60}-based OFET. d) The transfer characteristics I_{DS} vs. V_G plot of a C_{60}-based OFET under the forward and backward bias direction.

Output current is primarily determined by the dielectric constant of the dielectric layer; a high dielectric constant is typically preferred. **Figure 3**a presents the capacitances of albumen, PMMA, and PS, corresponding to driving frequencies of 200 Hz to 1 000 000 (1 M) Hz at 25 V. The devices for the measurement of capacitance had the metal–insulator–metal (MIM) configuration: Au/dielectric (400 nm)/indium tin oxide (ITO)/glass substrate. The capacitance of albumen is in the range 12.45–13.25 nF cm^{-2}, that of PMMA is 7.0–7.9 nF cm^{-2}, and that of PS is a constant 6.5 nF cm^{-2} for the different driving frequencies. The dielectric constant, ε, of albumen was 5.3–6.1, consistent with the value for denatured egg white, $\varepsilon = 5.2 \pm 0.7$, obtained by Lu et al.[20] The dielectric constant of albumen estimated from the result in Figure 3a was roughly double that of PMMA and PS.[21] As shown in inset of Figure 3a, the output current of pentacene-based OFETs of albumen dielectrics was also double that of devices with PMMA dielectrics and much higher than PS dielectrics (with the same thickness, 400 nm). The high dielectric constant of albumen is one of its advantages in OFET applications.

The influence of the albumen dielectrics on the capacitance in different environments was investigated. The MIM devices were separately stored in a nitrogen-filled box (relative humidity (RH%) < 0.1%), an ambient environment (RH% = 40–50%), and a container with the saturated water vapor (RH% > 90%) at room temperature. The capacitances were measured at a frequency of 5 KHz, biased at 10 V, as a function of storage time. As depicted in the Figure 3b, the change in the capacitance of chicken albumen dielectrics stored inside the glove box and in ambient atmosphere are small, within 5% of variations after 60 h of the storage time. The capacitance has a slight decrease (<10%) for the MIM device stored in a container with the saturated water vapor. These observations indicated the capacitances of the albumen dielectrics remain stable in a wide range of RH%, which presumably can be attributed to the hydrophobic properties of the albumen dielectrics after the thermal treatment.

The surface roughness of the dielectric layers and morphology of the organic semiconductor with dielectric layers also influence the performance.[22,23] **Figure 4** shows the topological atomic force microscopy (AFM) images of the albumen surface and 30-nm-thick pentacene deposited on the surfaces of the albumen, PMMA, and PS dielectrics in an area of 2.5 µm × 2.5 µm. The root mean square (RMS) roughness of the albumen dielectrics was 1.55 nm. The grain size of pentacene on the albumen dielectrics was 0.7–1.0 µm and those of PMMA and PS were 0.5–1.5 µm and 0.2–0.4 µm, respectively. Without optimizing the organic film growth, the crystallinity of pentacene on the albumen dielectric was comparable to that on the PMMA dielectric, which is one of the commonly used polymer dielectrics materials for OFETs.

Albumen dielectrics are suitable for the fabrication of flexible OFETs. The albumen is cast on ITO-patterned polyethylene

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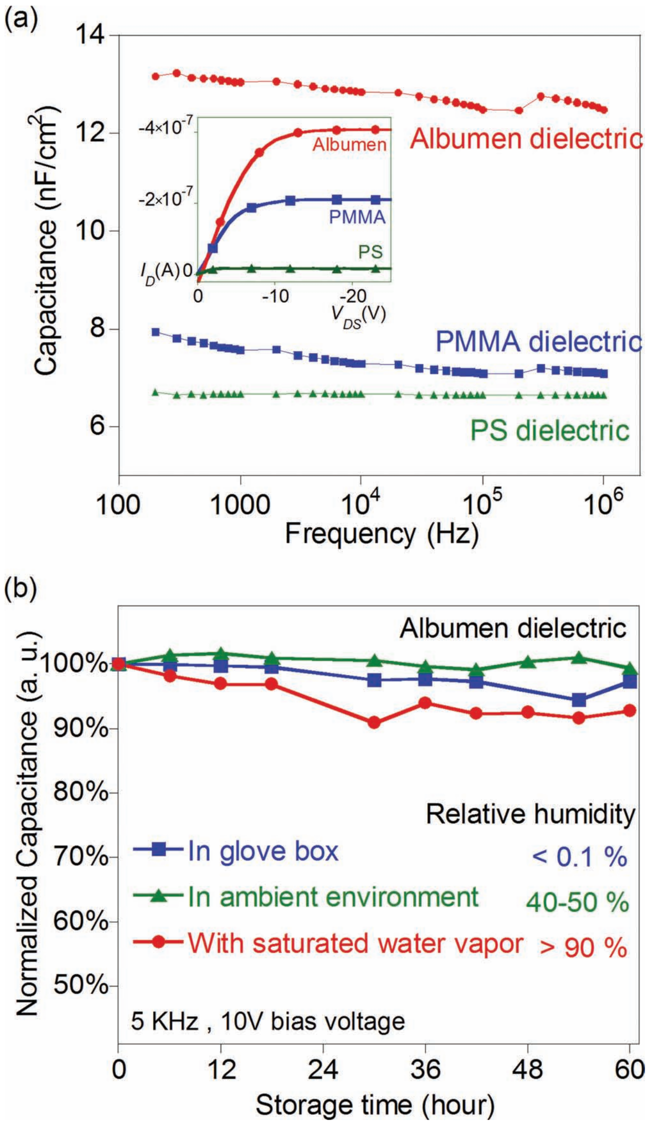

Figure 3. a) *C–V* characteristics of the MIM devices of albumen, PMMA, and PS with the thickness 400 nm and a capacitance area 2 mm × 1 mm, measured in the frequency range 200–1 M Hz. The inset shows the output currents of pentacene-based OFETs with albumen, PMMA, and PS dielectrics. b) Normalized capacitance of the albumen MIM devices measured at a frequency of 5 KHz as a function of storage times (h) in a nitrogen-filled glove box, in an ambient environment, and in a container saturated with water vapor.

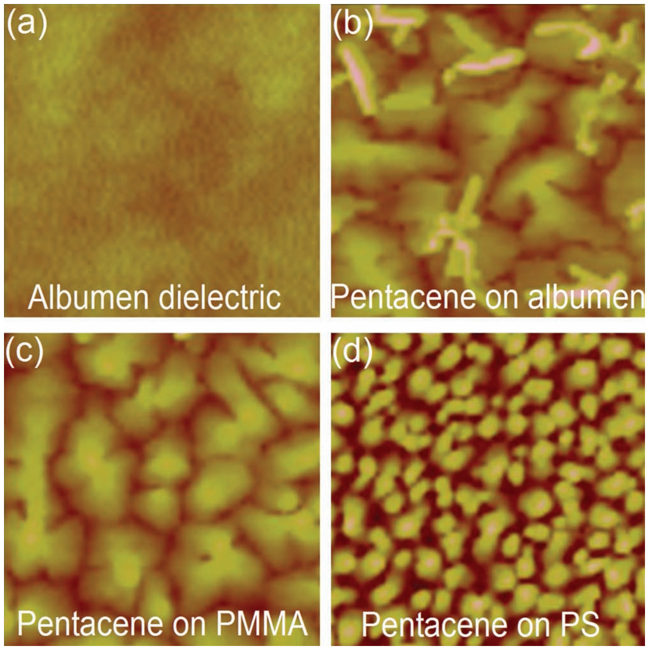

Figure 4. AFM tapping mode images of a) albumen and 30-nm-thick pentacene deposited on the surface of b) albumen, c) PMMA, and d) PS dielectrics. The dimensions of the AFM images are 2.5 μm × 2.5 μm.

naphthalate (PEN) substrates. **Figure 5**a presents a photograph, a schematic device configuration, and the output and transfer characteristics of a C_{60} n-channel OFET on an ITO-coated PEN substrate of albumen dielectrics. As shown in the photograph, the flexible OFETs can be easily bent to various curvatures. The output characteristics of flexible OFETs present an output current of 2×10^{-6} A at $V_G = 25$ V, similar to the devices fabricated on the rigid glass substrate. When the flexible OFET was bent to a radius of 0.5 cm several times, the magnitude of the output current remained at the same level, but the on/off ratio decreased, probably due to the increase in the leakage current after bending.

The albumen dielectrics-based complementary inverters were also fabricated in this study. Figure 5b depicts the circuit diagram and electrical transfer characteristics of a complementary inverter made of a pentacene p-channel OFET and a C_{60} n-channel OFET with albumen dielectrics operated at supply voltages (V_{DD}) equal to 15 V and 20 V. The structures of the individual pentacene p-channel OFET and the C_{60} n-channel OFET are shown in Figure 1a. The inverted output voltage was 7.2 V when $V_{DD} = 15$ V and 10.6 V when $V_{DD} = 20$ V. The gain reached a level of 15.3 and 20 for V_{DD} equal to 15 V and 20 V, respectively.

This work used a biomaterial, chicken albumen, as the gate dielectric in OFETs. Without further extraction or purification, albumen is more easily obtained, processable, and inexpensive than other biomaterials for OFET devices. The entire process for preparing the albumen dielectrics utilizes the properties of natural albumen without synthesis. The albumen dielectric presents the promising functions in fabricating both p-type pentacene and n-type C_{60} OFETs. 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. Moreover, the fabrication of applying albumen dielectrics for flexible OFETs and the complementary inverters demonstrated in this study exhibited decent device performance. The OFETs of albumen dielectrics achieved double the magnitude of the output current of devices with PMMA dielectrics because the dielectric constant is twice as large. Application of the native biomaterial to achieve low-cost fabrication without sacrificing device performance is successfully demonstrated. Although the chicken albumen dielectrics reported in this study were prepared by the thermally treated process, it is anticipated that the albumen dielectrics could have photodefinable properties, when a suitable

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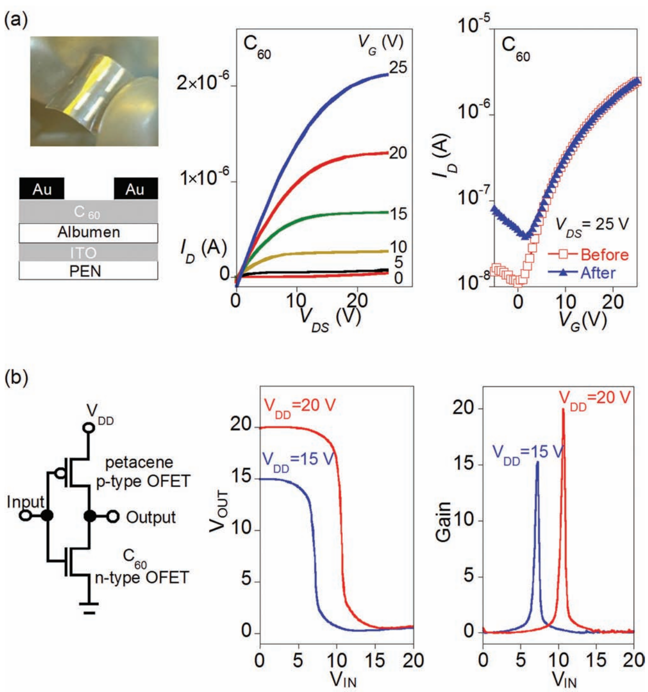

Figure 5. a) A photograph, a schematic of the device configuration, the output characteristics, and the transfer characteristics of a C_{60} n-channel OFET fabricated on an ITO-coated PEN substrate of albumen dielectrics. The transfer characteristics curve of the device before and after bending the flexible substrate to a radius of 0.5 cm several times is presented. b) Circuit diagram and electrical transfer characteristics of a complementary inverter made of a pentacene p-channel OFET and a C_{60} n-channel OFET with albumen dielectrics operated at the supply voltages (V_{DD}) equal to 15 V and 20 V.

photosensitive or photoinitiated additive is found and used for photoactivated denaturation and cross-linking in natural proteins. Accordingly, efforts to understand the egg white components, protein-protein interactions, denaturation by the thermal- and photoactivated process, and the influence of amino acid side chains under the electrical bias are currently underway and will hopefully lead to a more convenient and direct approach to use a chicken albumen in organic electronics. In addition, for the practical application of chicken albumen dielectrics as the alternative dielectric material, the intrinsic properties such as the stability, aging effect, tolerance to temperature and moisture, loss factor under different frequency regime, etc., should be investigated and this is currently underway.

Experimental Section

Materials and Sample Preparation: Pentacene and C_{60} were purchased from Aldrich and used without further purification. ITO glasses (RITEK Corp) were cut to 20 mm × 25 mm and were etched to leave an area of 1.5 m × 25 mm as a gate electrode. After cleaning the glass with detergent, deionized water, acetone, and isopropyl alcohol in an ultrasonic bath, the surfaces of the patterned ITO glasses were cleaned in a UV-ozone cleaner. Flexible conductive plastic substrates are purchased from Peccell Technologies, Inc.; these were 200 μm-thick PEN films coated with ITO of conductivity less than 15 Ω cm^{-2}.

Figure 1a shows the OFETs device configuration, which was constructed on a patterned ITO glass substrate as the gate electrode. Albumen liquid was obtained from chicken eggs purchased at a supermarket using a stainless steel mesh spoon to separate the egg yolk. The albumen was spun at 4000 rpm on the cleaned ITO substrates. The baking process of albumen films was 100 °C for 10 min, 120 °C for 10 min, and 140 °C for 10 min. The baked albumen dielectric layer was roughly 400-nm-thick, as measured by a surface profiler (Alpha step IQ, KLA-Tencor, USA). Pentacene and C_{60} (60-nm-thick) were vacuum thermally deposited at 10^{-6} Torr in the rate of 0.5–1 Å s^{-1}. The top-contact electrodes (40-nm-thick) were deposited by evaporating gold through a shadow mask with channel length (L) and width (W) defined as 100 μm and 1000 μm, respectively.

Characterization: Electrical characterization of pentacene and C_{60} OFETs and inverters was carried out at room temperature in a nitrogen-filled glove box with oxygen and moisture levels <1 ppm. The performance of OFETs and inverters was characterized using a probe station equipped with a semiconductor parameter analyzer (HP 4145B, Agilent Technologies). The capacitance of the dielectrics was measured inside the same nitrogen-filled glove box for devices of the MIM structures with a precision capacitance meter (HP 4284A Precision LCR meter, Agilent Technologies) under a bias voltage of 25 V plus a modulated voltage of 100 mV with driving frequencies 200 Hz to 1 M Hz. The electrical characteristics during the measurements of OFETs, inverters, and the capacitance of dielectrics were stable due to the dry, inert, and controlled atmosphere inside the glove box. AFM images were acquired using a NanoScope IIIa (Digital Instruments Inc., United States) in tapping mode.

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