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Lifetime improvement of organic light-emitting diodes with a butterfly wing's scale-like nanostructure as a flexible encapsulation layer

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ABSTRACT

Biomimetic nanostructures like butterfly wing's scale were fabricated with an anodic aluminum oxide (AAO) nanoimprint lithography technique. This bio-inspiration nanostructure exhibits an intrinsic hydrophobic property and thus was applied as a flexible encapsulation layer in organic light-emitting diodes (OLEDs) to improve device's lifetime. A ~80% enhancement on lifetime was obtained with simply imprinting the biomimetic nanostructures onto the flexible substrates. Our work provides a simple encapsulation approach for OLEDs, especially for flexible OLEDs.

1. Introduction

Biological cuticular microstructures or surface morphologies provide many intriguing photonic functions in polarization [1], structural color [2,3], and antireflection [4,5]. Recently, these cuticular micro- or nanostructures have been employed as inspiration in display applications. For instance, nanonipple arrays fabricated with interference lithography [4], e-beam lithography [6], selfmasked dry etching [7], nanoimprint [5,8], or bio-templates [8,9] have been used as antireflective structures in display systems. Nanostructures observed on a firefly lantern and its biological inspiration can generate a high transmission, which was used to efficiently enhance the luminous efficiency in light-emitting diode (LED) illumination [10]. Moth-eye-like quasirandom nanostructures have also been employed to enhance external quantum efficiency in flexible organic light-emitting diodes (OLEDs) through enhancing out-coupling of the waveguided light, reducing ohmic losses in the nanoimprinted process, broadening the periodicity and randomizing the emission directionality [11,12]. However, we notice that the influence of biomimetic nanostructures on optoelectronic device's lifetime has not been reported up to now although there have reported a lot of encapsulation work with micro- or nano-stratified film [13–15].

In this work, we constructed array structures like trogonoptera brookiana (a kind of butterfly) wing's scale with anodic aluminum oxide (AAO) templates and investigated this periodic array's influence on OLED's lifetime. It is worth noting that the wing's scale structures of trogonoptera brookiana exhibit an intrinsic superwater-repellent property, thus decreasing water permeability. Similarly, our bio-inspiration nanostructures also show a hydrophobic feature. By imprinting this biomimetic structure onto the flexible polyethylene terephthalate (PET) substrates as an encapsulation layer, we got 60–80% lifetime enhancements of OLEDs under a variety of environments.

2. Experimental details

2.1. Fabrication of polystyrene array

Polystyrene (PS) with a molecular weight of 10^5 g/mol was dissolved in the xylene with concentrations of 160, 330, 500, 660,

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and 1000 mg/ml and then left for 24 h for full dissolution before forming PS films onto cleaned PET substrates. Note that the PET substrates were first cleaned in sequence with ethanol and deionized water, and then blown with a nitrogen gas. Following that, the PET substrates were spin-coated with the PS solutions with a speed of 2000 rpm for 60 s and then covered with AAO templates (Whatman Int. Ltd., England, 13 mm diameter). With a 24 h drying process in a glove box, the AAO templates were finally removed with hot NaOH aqueous solution, forming a PS nanostructure array. Measurement on the hydrophobic property of the nanoimprinted PS films was completed with Easy Drop contact angle (CA) measurement system.

2.2. OLED fabrication

Prior to device deposition, the opposite sides of the PET substrates without PS arrays were cleaned with ethanol and deionized water, and then dried in an oven at 80° centigrade. And then these PET substrates were transferred into a vacuum chamber to thermally evaporate OLED with a device structure of Ag (80 nm)/MoO_x (2 nm)/N,N,N′,N'-tetrakis (4-Methoxy-phenyl) benzidine (MeO-TPD): 3 wt% 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F_4-TCNQ) (30 nm)/MeO-TPD (10 nm)/4,4′,4″-Tris (carbazol-9-yl)-triphenylamine (TCTA):bis (3,5-difluoro-2-(2-pyridyl) phenyl-(2-carboxypyri-dyl) iridium (III) (FIrpic, 8 wt%)/TCTA:Bis(2-methyldibenzo [*f*,*h*]quinoxaline) (acetylacetonate) iridium (III) [Ir $(MDQ)_2$ (acac), 3 wt%]/TCTA:FIrpic (8 wt%)/4,7-diphenyl-1,10-phenanthroline (Bphen) (10 nm)/Bphen: 3 wt% Li (20 nm)/Sm (4 nm)/Ag (14 nm). Here, the thick Ag and the thin Sm/Ag bilayer are the reflective anode and the semitransparent cathode, while MoO_x/MeO-TPD:F_4-TCNQ, MeO-TPD, Bphen and Bphen:Li are sequentially used as the hole injection bilayer (HIL), the hole transport layer (HTL), the electron transport layer (ETL), and the electron injection layer (EIL), respectively. The emission layers (EMLs) are adopted with triple-layer structures of TCTA:FIrpic/TCTA:Ir $(MDQ)_2$ (acac)/TCTA:FIrpic, where the FIrpic and Ir $(MDQ)_2$ (acac) phosphors act as blue and orange emitters. The device with nanoimprinted PS film on the PET substrate is denoted as A, while the control device without PS film is named B. All layers were thermally evaporated in a high vacuum system under a pressure of less than 5×10^{-4} Pa. The deposition rates of the organic layers and the electrodes were about 0.1–0.2 nm/s with quartz crystal oscillators. After completing the fabrication process and cooling for about 1 h, the devices were transferred into a glove box and encapsulated with glass covers. The electroluminescent (EL) characteristics including current and brightness were measured with a Keithley 2400 and a Spectrascan PR655 spectrophotometer.

2.3. Calculation of water permeability

A 150-nm thick Ca film was thermally deposited onto the PET substrate nanoimprinted with the PS array. Note that the Ca film and the PS array were located on the two sides of the PET substrate. Then the Ca film was encapsulated with a glass cover, leaving water permeate only from the PS array side. The water permeability was calculated by observing the change of the Ca film's color through microscope and calculating the reaction area with a home-made Matlab program (See Supplementary Material). The devices with or without an encapsulation PS array were laid into different environments and then measured once every day to test their lifetime. Note that we maintained a same driven current during the lifetime tests, with which an initial luminance of 1000 cd/m^2 was obtained.

3. Results and discussion

3.1. Hydrophobic features

From the manufacture procedure of the AAO-imprinted PS films shown in the schematic diagram of Fig. 1(c–f) and detailedly introduced in Section 2.1, we found that the imprinted PS films show a honeycomb-like array nanostructure (Fig. 1(g)) after etching the AAO template (Fig. 1(h)) from the PS film's surface. The honeycomb-like array nanostructure looks extremely like the microstructures of trogonoptera brookiana wing's scale, with the hole's size decreases from hundreds of nanometers to ~100 nm with a periodicity of 150–200 nm. Microcavities existing on Trogonoptera brookiana's wing scales may be the origin for the superhydrophobicity of their wing surfaces, so we measured the hydrophobic property of our nanoimprinted PS films and found the nanoimprinted PS arrays exhibit slightly different hydrophobic features with PS concentrations, with the CAs of 107, 123, 116, 105, and 89° for the PS solutions of 160, 330, 500, 660, and 1000 mg/ml, respectively, as shown in Fig. 2. With a PS solution of 330 mg/ml, we acquired a pretty good hydrophobicity with a CA of 123° (Fig. 1(i) and (j)), thus we finally employed the array with 330 mg/ml PS concentration to fabricate encapsulation films in our OLEDs. Actually, these nanostructure arrays look more like inverted nanocones with depths of 20 ± 10 nm, measured by atomic force microscope and stylus profiler.

3.2. Water permeability

It should be pointed out that PS is not an ideal material for device encapsulation because of relatively high water and oxygen permeability in polymer materials. However, the biomimetic PS array in this paper showed a pretty good hydrophobicity, therefore we tried to use it as an encapsulation film in OLEDs by imprinting it on the flexible PET substrate. As described in Section 2.3, a Ca film etching method was utilized to calculate water permeability of the nanoimprinted PS array with a Matlab program shown in Supplementary Material. Here, a 150-nm thick Ca film was thermally deposited onto the PET substrate and then the Ca-covered PET was encapsulated with glass. Note that the PS array had already been imprinted onto another side of the PET substrate in order to observe the permeability of water. Ca will react with H_2O in the air and generate $Ca(OH)_2$ and H_2, thus exhibiting color alteration. By observing the change on the color through microscope and calculating the reaction area with our home-made Matlab program, we estimated the water permeability of the PS array is 0.017 g/m^2/day, showing a 26% decrease compared to 0.023 g/m^2/day in an array-free PS structure.

3.3. Improvements on lifetime

Preventing water vapor's penetration into OLEDs may effectively improve device lifetime because water plays an important role in degrading the device performances [16]. To investigate the influence of the nanoimprinted PS array on device's lifetime, we deposited OLEDs onto the flexible PET substrate with a final 1 mm thick glass encapsulation layer onto the flexible OLED. The imprinted PS array is on the other side of the PET substrate, acting as an encapsulation film. Detailed device and encapsulation structure are shown in Fig. 3, in which we utilized a top-emitting OLED structure with triple-EMLs of TCTA:FIrpic (I)/TCTA:Ir $(MDQ)_2$ (acac) (II)/TCTA:FIrpic (III). Note that the blue EML in region III corresponds to a major exciton recombination region, and even with such a structure by locating blue phosphors into the major exciton recombination, device usually emits warm-white emission