Extended Abstracts of the 2020 International Conference on Solid State Devices and Materials, VIRTUAL conference, 2020, pp417-418

A versatile structure of light-emitting electrochemical cells for printed electronics

Yuki Tanaka[1], Jiang Pu[1] and Taishi Takenobu[1]

[1] Nagoya University
Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603, Japan
Phone: +81-52-789-5165 E-mail: tanaka.yuki@e.mbox.nagoya-u.ac.jp

Abstract

We propose a versatile Light-emitting Electrochemical Cell (LEC) structure that is easily prepared by laminating plastic films and drop-casting organic solutions. This simple fabrication allows us to realize various colored LECs with arbitrarily patterned light-emitting shapes. Moreover, the proposed structure is advantageous for building LECs using a solution-based process because of the absence of severe material/metal patterning. Thus, it presents a new approach for developing flexible printed devices.

1. Introduction

Organic light-emitting devices have been investigated intensively for constructing future functional lighting sources due to their inherently soft nature and the low-cost solution-based processability. The recent emergence of light-emitting electrochemical cells (LECs) has offered an easy method for fabricating organic light-emitting devices [1]. LECs are simply composed of two metal electrodes and a single active layer, which is a mixture of an electrolyte and a fluorescent molecule. Conventional LEC structures can be roughly divided into two types. One is the planar type, shown in Fig. 1(a), in which LECs are fabricated by simply depositing active materials onto substrates with horizontally pre-prepared electrodes [2]. However, the device is seriously limited in terms of scalability and patternability and is unsuitable for commercial applications. The second type is the sandwich-type LEC, depicted in Fig. 1(b) [3]. Although Most LECs are fabricated using this device structure, this device structure must deposit top metal electrodes onto active fluorescent materials as the final fabrication step, which makes it difficult to prepare completely solution-processed printed devices. Therefore, establishing additional simple and versatile LEC structures is sorely needed.

In this work, we propose a vertical LEC structure, as shown in Fig. 1(c), which utilizes both the planar-type simplicity and the sandwich-type assembly [4]. Because of this simplicity, the proposed LEC can be fabricated in two steps: 1) laminating plastic films onto arbitrary substrates and 2) solution-depositing light-emitting materials onto pre-prepared substrates. In addition to the simple fabrication, we can pattern light-emitting shapes/forms by simply manipulating the plastic films and integrating the devices without extra metal deposition and/or wiring. To prove this device strategy and confirm the light-emitting capability, we constructed vertical LECs with several polymers and observed various straight line–shaped colored-light emissions. Importantly, we can easily control the luminescent regions and shapes in the proposed structure.

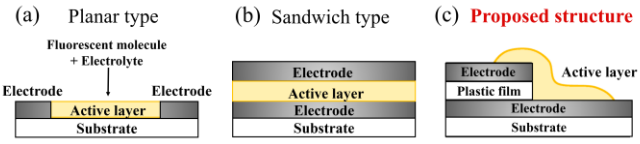

Fig. 1. (a) Schematic of a planar-type LEC. (b) Depiction of a sandwich-type LEC. (c) Illustration of the proposed LEC structure. Two electrodes are separated by plastic film, and the active layer is constructed on the step between the two electrodes.

2. Experiments

Device Fabrication

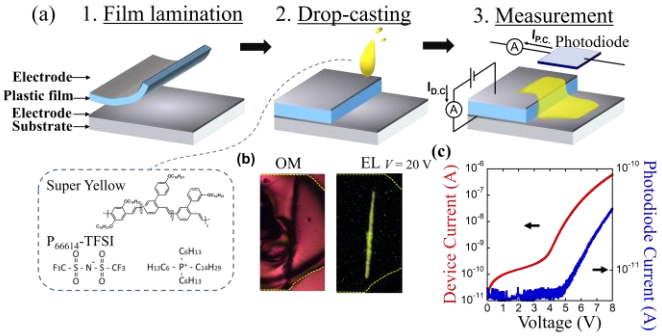

Fig. 2. (a) Schematic flow of the fabrication procedures for the proposed LEC. (b) Optical micrograph and EL image. A straight line-shaped yellow-light emission, which corresponds to the edge of the laminated PEN-film, was observed. (c) Device-current (red), applied-voltage, and photodiode-current (blue), *I-V-L*, characteristics.

All device fabrications and measurements were performed inside a nitrogen-filled glove box. Figure 2(a) shows the fabrication procedure of the proposed LEC. First, we deposited Au/Ni electrodes (Au/Ni = 50nm/3 nm) onto a glass substrate and polyethylene naphthalate (PEN) films. Next, we laminated the PEN substrate with the top electrode onto the glass substrate with the bottom electrode. Then the active materials were drop-casted onto the stepped area between the top PEN film and the bottom substrate, and the device was annealed at 120 °C for 30 min.

Measurement

The light emissions were measured with a voltage application via a source meter. A CCD camera and a Si photodiode were placed on top of the devices to detect the light emission, as the optical image, and the photocurrent, respectively. To clarify the detailed device operations, we simultaneously measured the device current (*I*) and the photodiode current. The photodiode current was proportional to the intensity of the emitted light (*L*).

Results and Discussions

Figure 2(b) shows an optical micrograph and an electroluminescence (EL) image. We could clearly confirm straight line–shaped yellow-light emissions from the edge of the PEN film, suggesting the formation of *p-n* junctions along the cliff edge of the PEN-film separator. Figure 2(c) displays the applied-voltage (V) dependences of the device current, and the photodiode-current (I-V-L) characteristics of a fabricated LEC. When V was relatively low (< 5 V), we observed a small increase in the device current without light emission, indicating that the observed current was the ion-displacement current. Meanwhile, when a higher voltage was applied (> 5 V), an enhanced device current and photodiode current were both detected. These observations confirmed the recombination of holes and electrons, due to the electrochemical-induced *p-n* junctions along the cliff edge of the PEN-film separator. Consequently, we successfully realized LECs using the proposed simple structures and easy fabrication methods.

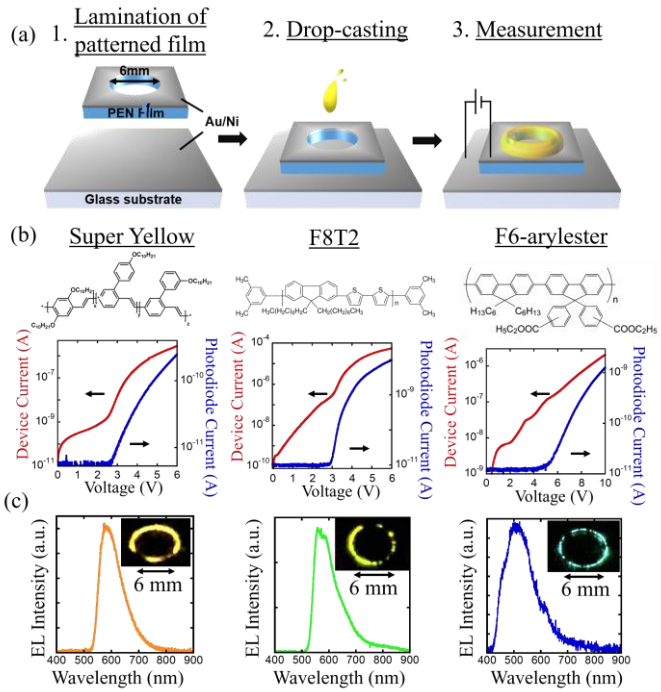

Fig. 3. (a) Schematic flow of fabrication procedures. (b) I-V-L characteristics of LECs based on SY-PPV (left), F8T2 (center), and F6-arylester (right). The chemical structures of these polymers are also shown. (c) EL spectra obtained from SY-PPV, F8T2, and F6-arylester. The insets show direct observations of EL images.

Next, we demonstrated various colored LECs by molding light-emitting regions into a circular shape to expand the applicability of the proposed structure. As shown in Fig. 3(a), we made 6-mm-diameter holes in 16-μm-thick PEN films using commercial punch tools and deposited Au/Ni electrodes. As the fluorescent materials, we selected SY-PPV, poly(9,9-dioctylfluorene-co-bithio-phene) (F8T2), and poly(fluorine-co-arylfluorene) with an ethyl ester group on the arylfluorene unit (F6- arylester), and P66614-TFSI as the electrolyte [5-7]. Finally, we drop-casted a solution of active materials to cover the hole in the plastic film.

Figure 3(b) presents the I-V-L characteristics of each polymer LEC. We can confirm a significant enhancement of both the device current and photodiode current while biasing a few volts, indicating the EL generation in all devices. Moreover, the relative threshold voltages of SY-PPV, F8T2, and F6-arylester qualitatively agree with the HOMO–LUMO gaps of these materials [5-7]. Figure 3(c) shows direct observations of the EL images and EL spectra. Because we needed to apply very high voltages to take EL images, we prepared different devices and measured EL spectra with a spectrometer. As shown in Figs. 3(c), the yellow, yellow-green, and blue light emissions can be observed. All luminescent shapes were well controlled by the shapes of the holes molded in the laminated PEN film, proving the high patternability of the proposed device strategy. At the session, we will report on the results and discussions in more detail.

3. Conclusions

We proposed a simple and versatile LEC structure that required only two steps to realize light-emitting devices. The proposed structures can independently determine the lighting shape (via film pre-patterning) and EL color (via material selection) without the complicated stacking or wiring of active materials and electrode metals. This is suitable for solution-based fabrication processes. For instance, one-step inkjet printing of light-emitting solutions on scalable and assembled plastic films/substrates could be a feasible approach to developing flexible and printed light-emitting devices, based on LECs.

Acknowledgements

Y.T. acknowledges support by WISE Program (Doctoral Program for World-leading Innovative & Smart Education), Nagoya University from the Ministry of Education, Culture, Sports, Science and Technology. J.P. was support by JSPS KAKENHI (Grant Numbers JP19K15383 and 20H05189). T.T. was support by JSPS KAKENHI (Grant Numbers JP26102012, JP25000003, 19K22127, and JP17H01069), and was also supported by JST CREST through Grant Number JPMJCR17I5, Japan.

References

[1] Q. Pei, G. Yu, C. Zhang, Y. Yang, and A. J. Heeger, Science **269**, (1995) 1086.

[2] T. Sakanoue, K. Sawabe, Y. Yomogida, T. Takenobu, S. Seki, and S. Ono, Appl. Phys. Lett. **100**, (2012) 263301.

[3] K. Sato, S. Uchida, S. Toriyama, S. Nishimura, K. Oyaizu, H. Nishide, and Y. Nishikitani, Adv. Mater. Technol. **2**, (2017) 1600293.

[4] Y. Tanaka, J. Pu, and T. Takenobu, Appl. Phys. Express (2020) DOI: 10.35848/1882-0786/aba56c

[5] T. Sakanoue, K. Sawabe, Y. Yomogida, T. Takenobu, S. Seki, and S. Ono, Appl. Phys. Lett. **100**, (2012) 263301.

[6] T. Sakanoue, F. Yonekawa, K. Albrecht, K. Yamamoto, and T. Takenobu, Chem. Mater. **29**, (2017) 1606392.

[7] G. Nagatsu, T. Sakanoue, S. Tane, F. Yonekawa, and T. Takenobu, Mater. Chem. Front. **2**, (2018) 952.