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Letter

Fully Recyclable OLEDs Built on a Flexible Biopolymer Substrate

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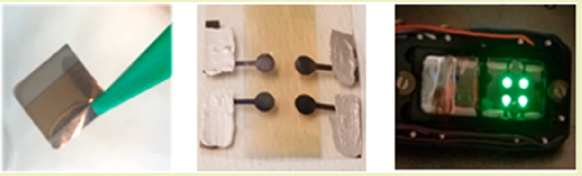
ABSTRACT: This is the "mobile" era, characterized by a growing demand of flexible substrates for novel products such as curved screens, folding smartphones, and wearable devices. In this framework, plastic electronics represents a suitable technology to replace silicon-based electronics. However, up to now, little attention has been devoted to rendering this technology more environmentally sustainable. It is thus necessary to develop new eco-designed devices that allow recycling of all the components and recovering the valuable materials through sustainable methods. For the first time, we report the fabrication of organic light emitting diodes made on an as-cast biopolymeric flexible substrate. Sodium alginate is a natural biodegradable polymer derived from brown algae; it is water-soluble and easy to manipulate for the realization of flat and transparent foils using an environmentally friendly process. Thus, the active stack can be directly deposited on the biopolymer substrate in a bottom-up architecture with no need for a pretreatment or a buffer layer. In addition, the devices can be disassembled and all of the valuable materials almost entirely recovered. This result opens up new and exciting opportunities for the fabrication of electronic and optoelectronic devices with a green platform for an ambient sustainable circular economy.



KEYWORDS: *Flexible electronics, Green electronics, OLED, Biopolymers, Disassembly and recycling, Environmental sustainability*

INTRODUCTION

Today, the global market of organic electronics totals many billions of dollars and is expected to further increase in the near future. In particular, there is a growing demand for flexible substrates for novel products such as curved screens, folding smartphones, and wearable devices. Therefore, scientific research is increasingly looking for innovative materials that can undergo a large mechanical deformation and yet be employed to realize high-performance devices.[1,2] In this framework, plastic electronics represents a forefront research area in order to replace the unsatisfactory technology based on silicon with a suitable one.

Among others, flexible organic light-emitting devices (OLEDs) are presently the basis of the latest generation of commercial displays, as they are flexible, thin, and light and have a reduced energy consumption. Flexible electronics can be fabricated using a bottom-up approach, in which all the functional and active layers, from metals to semiconductors, are sequentially grown directly on a flexible and transparent polymeric substrate. The devices now on the market are usually built on poly(ethylene terephthalate) (PET), a thermoplastic polymer characterized by excellent optical and mechanical properties. Organic semiconductors, either small molecules or polymers, make up the active regions while metals constitute the conductive parts.

However, despite the enormous efforts made, little attention has been devoted to render this technology more environmentally sustainable. On the contrary, electronic waste (e-waste) production is one of the fastest-growing pollution problems worldwide, given the large volume involved and the presence of a variety of toxic substances, which can contaminate the environment and threaten human health.[3] In fact, a proper management of the e-waste collection, which is at present carried out only in the more advanced countries, is not enough to avoid pollution. It is also necessary to develop new eco-designed and green devices that allow recycling of all the components and recovering the valuable materials through sustainable methods.

Substantial scientific research into these topics has started only recently. In particular, it has been focused on the use of materials, obtained from raw matter largely abundant in nature instead of fossil-oil derivatives, that either are biodegradable or can be reconverted with eco-sustainable processing methods.[4−6] The substitution of conventional materials with greener ones has been addressed with regard to all of the OLED components: namely the substrate, active layers, and conductive contacts. However, from a quantitative point of view, the most relevant component is represented by the substrate, which typically accounts for more than 90% of the total volume. Its substitution would therefore provide the

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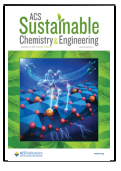

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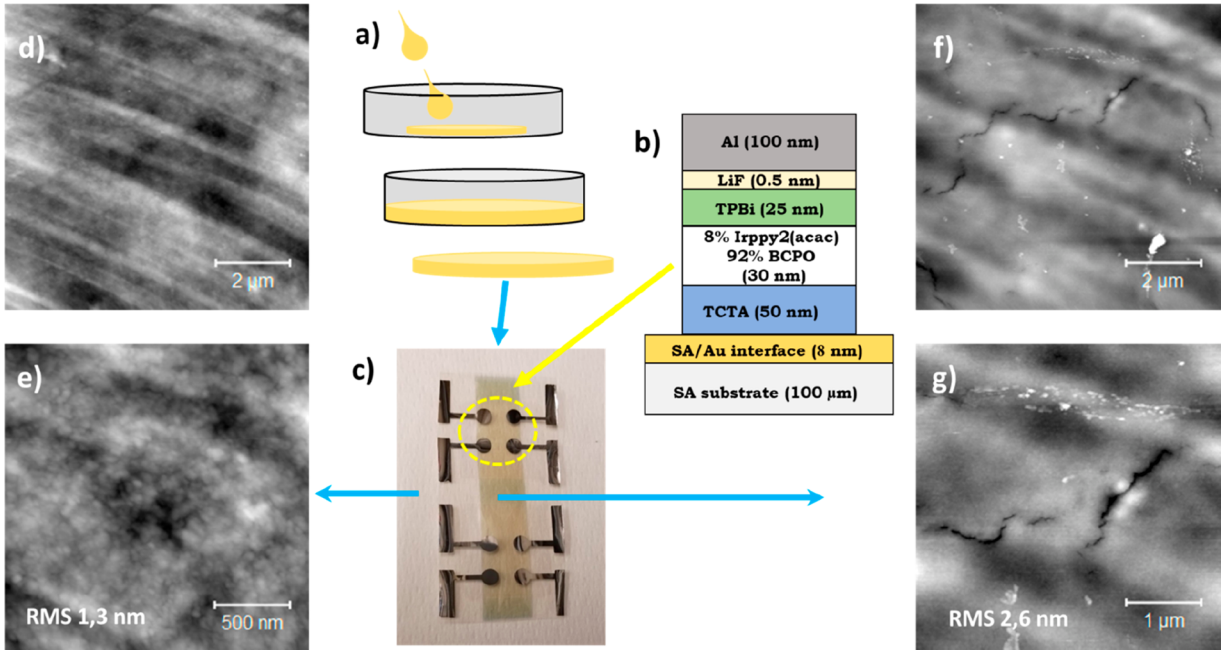

Figure 1. (a) Scheme of the process employed to realize the freestanding SA foils. (b) Layout of the device structure. (c) Photograph of an array of eight OLEDs: the Au stripe and the Al pads are visible on the SA foil. (d, e) AFM images of the pristine SA foil. (f, g) AFM images of the Au stripe surface. The false-color z scale is the same for all of the images and is equal to 20 nm, from black to white.

largest environmental impact, provided that no toxic substances are employed.

The most relevant results obtained with materials derived from renewable resources have been obtained with cellulose, chitin, and silk fibroin. In other cases reported in the literature, biopolymer films have been first deposited on glass or ITO to provide the necessary mechanical stability or conductive properties.[4] Therefore, only bacteria-derived cellulose nanofibers, nanofibrillated cellulose from wood, and chitin nanofibers have been successfully exploited to prepare flexible, freestanding, and highly transparent substrates.[7−9]

Due to their morphological characteristics, all of the freestanding substrates mentioned above present a surface with a roughness that is incompatible with the realization of small-molecule-based OLEDs in a bottom-up configuration. Specifically, OLEDs require a surface roughness of around 1 nm. Accordingly, working devices have only been reported for the case of chitin nanofiber films, where planarization is guaranteed by a thin layer of poly(methyl methacrylate), PMMA.[7] However, PMMA is not biodegradable, is not derived from renewable resources, and is not processable under environmentally friendly methods.

A better control of the surface roughness might be obtained using regenerated amorphous cellulose.[9] However, these foils present a substantially reduced transparency in the green−blue visible region, a strong limitation for the OLED performance. Working devices have been also successfully built on glass-supported cellulose nanocrystal based films.[10] In this case, the fibers are smaller in size in comparison to bacterial cellulose nanofibers and nanofibrillated cellulose, a fact that can provide a reduced surface roughness. Nevertheless, these films are still too fragile, even though glycerol has been used to plasticize them, and they cannot guarantee the required mechanical stability.

In conclusion, there is not yet a satisfactory example of a polymer derived from renewable resources, i.e. biodegradable and processable with eco-sustainable methods, used to realize freestanding and ready to use substrates to build a working OLED. Furthermore, with regard to recycling each single component, only a few papers have mentioned the possibility of device disassembly and recovery of valuable materials,[10,11] and only one has reported sufficiently detailed tests.[11] However, in the cited paper, the recycling method proposed is by no means sustainable, as it is based on the use of chlorinated aromatic compounds that are toxic substances.

In this work, we report, for the first time, the fabrication of an OLED directly grown on an as-cast biopolymeric flexible substrate. Sodium alginate (SA) is a natural biodegradable polymer derived from brown algae and is water-soluble, amorphous, and easy to manipulate, so that one can realize flat and transparent foils with an environmentally friendly process.[12] The flexibility, mechanical stability, and transparency of these foils are comparable to those of the best-performing cellulose and chitin nanofiber substrates. In addition, SA also meets the requirement of a fairly high refractive index,[13] necessary in OLEDs for an efficient light extraction.[14]

EXPERIMENTAL SECTION

SA foils have been obtained by casting a 4 wt % water solution of a pharmaceutical-grade product, used as purchased, into polystyrene Petri dishes.[15] The process is schematically drawn in Figure 1a. The evaporation of the excess water and the final drying were performed at room temperature under a controlled humidity of around 30%. The final thickness can be adjusted varying the total amount of the solution poured into the Petri dish. Substrates with balanced mechanical properties, in terms of stability and flexibility, and a transparency superior to 90% over the whole visible range can be realized with 30 g of solution into a 9 cm ϕ Petri dish. This volume yields a foil thickness of around 130 μm.

The refractive index of these foils has been measured by means of reflectance and transmittance spectroscopy associated with an integrating sphere and is equal to 1.55. This value is in good

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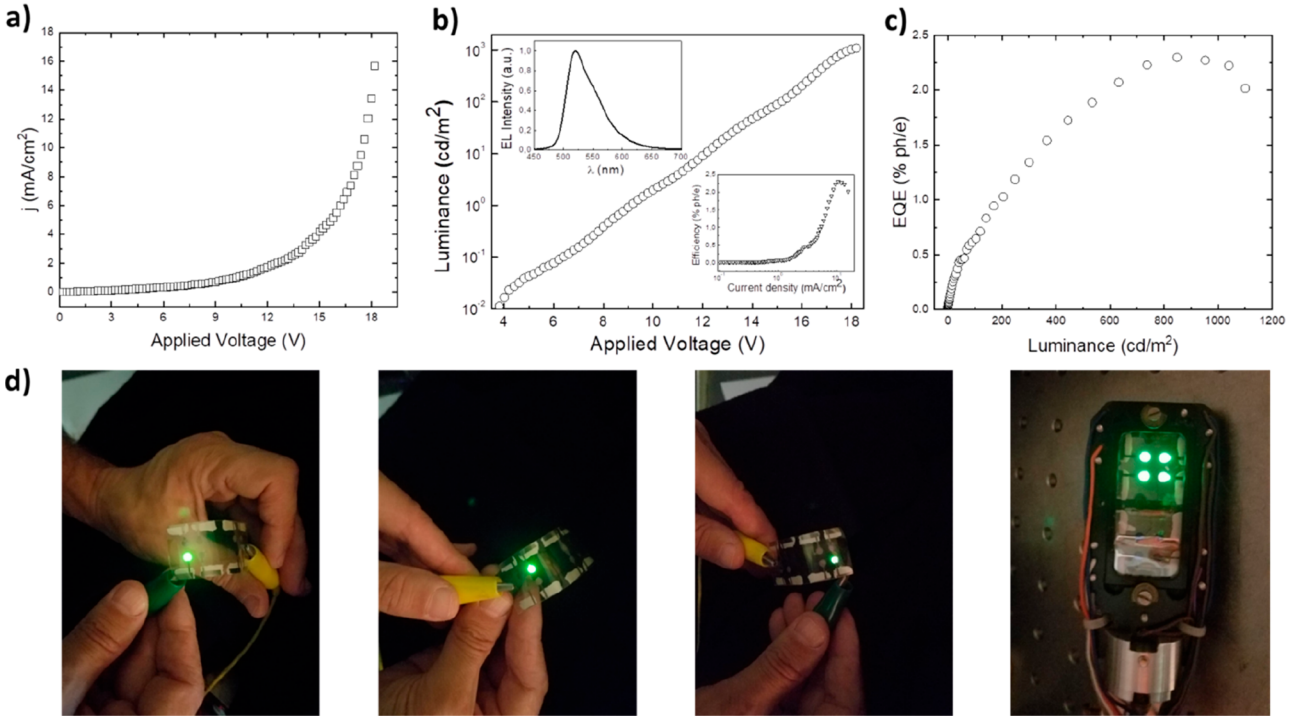

Figure 2. (a) Current density versus voltage curve. (b) Electroluminescence versus voltage characteristics (main panel), an external quantum efficiency versus current density curve (bottom inset), and an electroluminescence spectrum (top inset). (c) External quantum efficiency versus luminance curve. (d) Photographs of working OLEDs, operated in air and under bending conditions.

agreement with Cathell et al., who report 1.518,[13] whereas Esteban et al. have found 1.37.[16] This discrepancy may be due to the procedures adopted to isolate and purify SA. The refractive index may be further increased by introducing in the pristine SA solution variable amounts of nanoparticles having a larger refractive index.

A 8 nm thick gold (Au) layer was sputtered directly on the SA foil, to create the anode electrode.[15] Then, the active stack made of small-molecule layers was deposited via vacuum sublimation, as schematically reported in Figure 1b. The device structure was completed with the thermal sublimation of a 100 nm thick aluminum (Al) layer, patterned in order to realize eight devices.

See the Supporting Information for a detailed description of the fabrication process, materials, and instrumentation employed.

RESULTS AND DISCUSSION

OLED Characterization. In Figure 1c, an array of eight OLEDs is shown. The gray pads are the Al cathodes, whereas the yellow stripe is the common Au anode. This stripe has been sputtered on the foil side that has been in contact with the Petri dish bottom, as it is 1 order of magnitude smoother than the other.[15]

An atomic force microscopy (AFM) image, reported in Figure 1d, shows that the SA surface presents some features with a maximum height of 15 nm. This is due to the fact that it is a replica of the Petri dish bottom, in which the solution has been poured. In Figure 1e, we report an $2 \times 2\ \mu m^2$ image obtained by enlarging within the stripes. This area has a root-mean-square (RMS) roughness of 1.3 nm. A better control over the roughness could be achieved using a smoother mold; however, it is an acceptable value in order to grow a smooth stack of the active layers.

As described above, the anode is an Au stripe with a sheet resistance of 17 Ω/□, realized with a nominal thickness of 8 nm. This thickness value is chosen to combine a good electrical conduction and a minimum reduction of the transparency in the visible range.[12] The Au surface exhibits a morphology similar to that of pristine SA (Figure 1f,g) with a slight increase in roughness (2.6 nm, RMS). The presence of spikes, which may generate short-cut points as in the case of ITO,[17] was not observed. Very thin Au layers grow on a smooth polymeric surface such as SA, forming clusters with a preferential lateral direction.[18] Accordingly, the typical granular structure of Au films grown on hard inorganic substrates is not observed.[19] As reported elsewhere, for a thickness equal to or below 5 nm, the Au/SA interface is represented by an intermixed region, which forms during the sputtering process.[20] In this case, some cracks can be observed with a depth of below 3 nm. They form on the top of the intermixed region, where the Au film grows more homogeneously. Their presence, however, does not affect the electrical properties of the Au/SA stripe under bending conditions.[15]

In Figure 2a, a current density (J) versus voltage curve of a working OLED is reported. In Figure 2b, we report, for the same device, an electroluminescence (EL) versus voltage curve together with an EL spectrum (top inset) and an external quantum efficiency (EQE) versus current density curve (bottom inset). As expected, the EL spectrum reproduces the phosphorescence behavior of the emitter ($Ir(ppy)_2(acac)$). A maximum value of 1100 cd/m^2 for the luminance at 18 V and a maximum external efficiency of 2.3% at about 10 mA/cm^2 have been measured. Finally, an EQE versus luminance curve is shown in Figure 2c.

This EL performance is comparable with those of the best biopolymer OLEDs reported in the literature. However, the performance is obtained at higher voltage values in comparison to glass-based OLEDs.[4,21] In order to understand what causes this variation in the threshold voltage, a theoretical simulation has been performed using a modification of the Child's law.[22] An extended discussion of the model employed can be found

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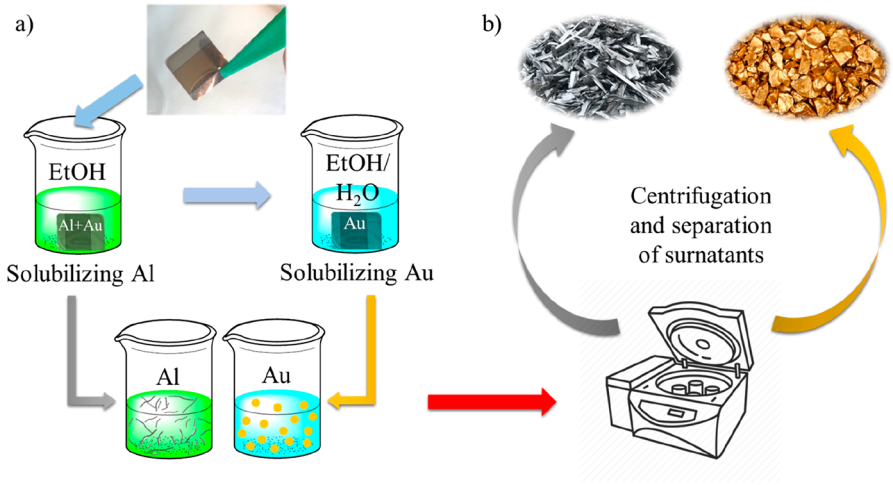

Figure 3. Procedure used to disassemble the device, from (a) to (b). The model system is first dipped into ethanol to solubilize Al and then in ethanol/water to solubilize Au. After centrifugation, the metals are finally recovered as precipitates, while the active components are solubilized in the solvents.

in the Supporting Information. The best fit of the data indicates the presence of three different threshold values. This behavior can be explained by assuming the presence of charge traps at the interfaces between the organic OLED stack and the injection electrodes. This topic is highly relevant for the optimization of the system and will be the subject of future work.

In Figure 2d, some photographs of OLEDs operating in air are displayed. The three photographs on the left show that the flexibility of the SA substrate allows the OLEDs to also work under bending conditions. In the photograph to the right, four devices are simultaneously operated.

Disassembly and Recycling. In order to prove the concept of ambient sustainability of the platform described herein, we have devised an original method using an eco-friendly process that allows a selective and effective recovery of all the components. In order to carry out a quantification of the materials recovered, we have realized a model system that reproduces the structure of an OLED, as reported in Figure 1b, but on a much larger scale. Our disassembly method is a two-step process and is based on the use of nontoxic solvents, such as water and ethanol (Figure 3). Ethanol is currently available from renewable resources (i.e., bioethanol). The model system has a total active surface of 3.20 cm^2, allowing a semi-quantitative evaluation of the recovery efficiency. To this purpose, the size of the SA substrate and the extension of the OLED stack area have been precisely measured. The thickness values of the Au and Al layers have been obtained through a calibration of the deposition rates as described in the Supporting Information.

In the first step, the sample is dipped into 5 mL of ethanol at room temperature. Al can be fully separated from the surface after 15 min of stirring with a magnetic bar or after 10 min in an ultrasonic bath (Elmasonic S40, 220−240 V, 50/60 Hz). Following this step, the SA foil with only Au left on top is withdrawn from the ethanol bath. Al and the active organic layers are now dispersed and solubilized in the solvent, respectively.

In the second step, the Au/SA bilayer can be separated in an ethanol/water (1/2) mixture. The sample is gently shaken at room temperature for a few minutes, with the help of a clump. Au can be thus dispersed in the liquid phase, while the SA film is only slightly swollen. The ethanol/water ratio of the mixture has been optimized to promote the Au separation while the SA solubilization is minimized. A higher presence of SA in the solution would increase the viscosity and would not allow an effective recovery of Au in the following centrifugation step. Thus, the SA film can also be entirely recovered (Figure S4).

The metals, separated in two different beakers, can be finally recovered from the two liquid phases with a centrifugation at 10000 rpm for 2 min (DIAB D30249 centrifuge), followed by decanting the two supernatants. Al and Au are collected as precipitates on the bottom of the two tubes, dried under vacuum for 3 days, weighed, and analyzed with inductively coupled plasma−optical emission spectrometry. The active organic components can be recovered from the supernatant after the evaporation of the solvents.

The values obtained have been compared with the deposited values, estimated from geometric considerations as described in the Supporting Information. The data indicate that we have obtained recovery efficiencies of 77% and 87% for Al and Au, respectively. These data can be considered very promising, as the uncertainty in the initial amounts present on the model system is relatively high. The optimization of the process will be the subject of future work.

CONCLUSIONS

Herein, we have reported the use of sodium alginate, a biodegradable polymer obtained from brown algae, to realize transparent, flexible, and ready to use freestanding substrates. In particular, this amorphous polymer allows solving the planarization and stability limitations of other natural materials, whose employment has been proposed in green electronics and optoelectronic applications. For the first time, we have successfully realized OLEDs operating under bending conditions, directly on top of a freestanding biopolymer foil. In addition, a recovery of nearly all of the valuable materials can be obtained using an environmentally safe disassembly method, thus avoiding the production of electronic or chemical waste. This approach opens up new, promising perspectives for the development of a green technology capable of lowering the energy consumption and the impact on the environment.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.1c03374.

Details of the OLED fabrication and materials employed, data regarding the optical characteristics of the samples, details of the electrical measurement setup, description of the theoretical simulations, scheme of the device model used for disassembly and material recovery evaluations (PDF)

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Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Yang, Y.; Gao, W. Wearable and flexible electronics for continuous molecular monitoring. *Chem. Soc. Rev.* **2019**, *48*, 1465−91.

(2) Gupta, S.; Navaraj, W. T.; Lorenzelli, L.; Dahiya, R. Ultra-thin chips for high-performance flexible electronics. *npj Flexible Electronics* **2018**, *2*, 1−15.

(3) Kiddee, P.; Naidu, R.; Wong, M. H. Electronic waste management approaches: an overview. *Waste Manage.* **2013**, *33*, 1237−50.

(4) Li, W.; Liu, Q.; Zhang, Y.; Li, C.; He, Z.; Choy, W. C. H.; Low, P. J.; Sonar, P.; Kyaw, A. K. K. Biodegradable Materials and Green Processing for Green Electronics. *Adv. Mater.* **2020**, *32*, 2001591.

(5) Piro, B.; Tran, H. V.; Thu, V. T. Sensors Made of Natural Renewable Materials: Efficiency, Recyclability or Biodegradability - The Green Electronics. *Sensors* **2020**, *20*, 5898.

(6) Pradhan, S.; Brooks, A. K.; Yadavalli, V. K. Nature-derived materials for the fabrication of functional biodevices. *Materials Today Bio* **2020**, *7*, 100065.

(7) Jin, J.; Lee, D.; Im, H.-G.; Han, Y. C.; Jeong, E. G.; Rolandi, M.; Choi, K. C.; Bae, B.-S. Chitin Nanofiber Transparent Paper for Flexible Green Electronics. *Adv. Mater.* **2016**, *28*, 5169−75.

(8) Legnani, C.; Villani, C.; Calil, V. L.; Barud, H. S.; Quirino, W. G.; Achete, C. A.; Ribeirao, S. J. L.; Cremona, M. Bacterial cellulose membrane as flexible substrate for organic light emitting devices. *Thin Solid Films* **2008**, *517*, 1016−1020.

(9) Zhu, H. L.; Xiao, Z. G.; Liu, D. T.; Li, Y. Y.; Weadock, N. J.; Fang, Z. Q.; Huang, J. S.; Hu, L. B. Biodegradable transparent substrates for flexible organic-light-emitting diodes. *Energy Environ. Sci.* **2013**, *6*, 2105−11.

(10) Najafabadi, E.; Zhou, Y. H.; Knauer, K. A.; Fuentes-Hernandez, C.; Kippelen, B. Efficient organic light-emitting diodes fabricated on cellulose nanocrystal substrates. *Appl. Phys. Lett.* **2014**, *105*, 063305.

(11) Zhou, Y.; Fuentes-Hernandez, C.; Khan, T. M.; Liu, J.-C.; Hsu, J.; Shim, J. W.; Dindar, A.; Youngblood, J. P.; Moon, R. J.; Kippelen, B. Recyclable organic solar cells on cellulose nanocrystal substrates. *Sci. Rep.* **2013**, *3*, 1536.

(12) Pawar, S. N.; Edgar, K. J. Alginate derivatization: a review of chemistry, properties and applications. *Biomaterials* **2012**, *33*, 3279−305.

(13) Cathell, M. D.; Schauer, C. L. Structurally Colored Thin Films of Ca2+-Cross-Linked Alginate. *Biomacromolecules* **2007**, *8*, 33−41.

(14) Park, C. Y.; Choi, B. Enhanced Light Extraction from Bottom Emission OLEDs by High Refractive Index Nanoparticle Scattering Layer. *Nanomaterials* **2019**, *9*, 1241.

(15) Maccagnani, P.; Bertoldo, M.; Dinelli, F.; Murgia, M.; Summonte, C.; Ortolani, L.; Pizzochero, G.; Verucchi, R.; Collini, C.; Capelli, R. Flexible Conductors from Brown Algae for Green Electronics. *Advanced Sustainable Systems* **2019**, *3*, 1900001.

(16) Esteban, O.; Marvà, F.; Martinez-Anton, J. C. Optical constants of a sodium alginate polymer in the UV-vis range. *Opt. Mater.* **2009**, *31*, 696−9.

(17) Kim, K.-B.; Tak, Y.-H.; Han, Y.-S.; Baik, K.-H.; Yoon, M.-H.; Lee, M.-H. Relationship between Surface Roughness of Indium Tin Oxide and Leakage Current of Organic Light-Emitting Diode. *Jpn. J. Appl. Phys.* **2003**, *42*, L438−440.

(18) Siegel, K.; Lyutakov, O.; Rybka, V.; Kolská, Z.; Švorčík, V. Properties of gold nanostructures sputtered on glass. *Nanoscale Res. Lett.* **2011**, *6*, 96.

(19) Zhang, Y.-W.; Wu, B.-Y.; Chen, K.-C.; Wu, C.-H.; Lin, S.-Y. Highly conductive nanometer-thick gold films grown on molybdenum disulfide surfaces for interconnect applications. *Sci. Rep.* **2020**, *10*, 14463.

(20) Capelli, R.; Maccagnani, P.; Dinelli, F.; Murgia, M.; Bertoldo, M.; Montecchi, M.; Doyle, B. P.; Carleschi, E.; Pasquali, L. Understanding adhesion of gold conductive films on sodium-alginate by photoelectron spectroscopy. *Thin Solid Films* **2019**, *690*, 137535.

(21) Liu, Y. Q.; Xie, Y. M.; Liu, Y.; Song, T.; Zhang, K. Q.; Liao, L. S.; Sun, B. Q. Flexible organic light emitting diodes fabricated on biocompatible silk fibroin substrate. *Semicond. Sci. Technol.* **2015**, *30*, 104004.

(22) Chu, T.-Y.; Song, O.-K. Thickness dependence of the trap states in organic thin film of N, N′-bis(naphthalen-1-yl)-N, N′-bis(phenyl) benzidine. *Appl. Phys. Lett.* **2007**, *91*, 073508.