

LOW-COST FABRICATION METHODS FOR ORGANIC/INORGANIC HYBRID OPTOELECTRONIC STRUCTURE ON A FLEXIBLE SUBSTRATE

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ABSTRACT

Developments in semiconducting nanostructures and organic polymers have opened new doors for optoelectronic devices. Simple fabrication steps make it easy to create large functional areas of these materials. This has made organic polymers a popular functional layer for organic light emitting diode (OLED) monitors, and quantum dots (QDs), popular for solar panels. Discoveries with both materials continue to be made, which improve their usability and efficiency. This paper presents our work on developing a hybrid organic non-organic functional light emitting device on a flexible substrate outside of a clean room, using only low-cost, benchtop machines. A simple, low-cost process allows for rapid device fabrication, which is more ideal for education and explorative research applications, as well as easier scaling for mass production. Results show characterization of emissive areas and spectrum for the devices. A difference in emission spectra between devices with and without quantum dots is noticeable, proving that optoelectronic devices can be made with MEH-PPV and QDs with simplified fabrication techniques. The work is concluded with a short discussion on how fabrication methods dictate device performance.

1 INTRODUCTION

Flexible electronics are introducing a new era of convenience in computing and sensing [1]. Thin, flexible devices can exist outside of rigid casing to function on contoured, moving surfaces. As an example, wearable optical sensors can collect physiological data with minimal effort required from the subject. Blood Volume Pulse (BVP) is a common, optical method for measuring heart rate. Through contact with human skin, a typical reflective BVP sensor uses an adjacent light source and photodetector pair to emit infrared light into the skin, and detect the amount that is reflected back. This type of sensor is used for both health and cognitive state monitoring purposes [2,3]. Existing BVP sensors function either with red or infrared light. These sensors typically use a clip or strap to stay secured to a subject's finger on one hand, and provide reliable information when that hand is not moving [4]. Both health and cognitive monitoring fields would benefit from a sensor that did not have this constraint, allowing subjects to be active during data collection. A new generation of wearable optical sensors will benefit from small, flexible, energy efficient light sources that are very simple to produce.

Both quantum dot nanocrystals and organic polymers have optoelectronic properties that make them key players in the field of flexible, optical electronics [5,6]. Organic polymers have been proven to serve as efficient light emitting diodes through a multi-layer process. The first, functional layer, can emit light through the decay of excitons, the formation of which are boosted by the second, hole

injection layer [7]. Quantum dots, through the effect of quantum confinement, are capable of emitting light when power is applied [6]. The quantum confinement effect in QDs is size tunable, meaning they can be grown to absorb and emit the desired wavelengths of light ranging from the visible to the infrared [8,9]. Introducing alloying into the growth process allows QD quantum confinement effect to be tunable by composition rather than size, which allows for easier integration into optoelectronic devices [10]. Compared to functional layers consisting only of QDs, a hybrid layer of quantum dots in an organic polymer creates devices that are more efficient, operating at lower voltages [11]. Work with organic polymers has shown that simple methods, that avoid clean room processes such as photolithography, can produce light emitting diodes on a glass substrate [12, 13]. The aim of this work is to explore how organic polymers and alloyed quantum dots, using simplified fabrication methods, can produce flexible light emitting diodes.

The light emitting device consists of a multilayered, sandwich structure. The main, functional layer is a blend of the organic polymer MEH-PPV, and CdSe/ZnS alloyed quantum dots, tuned to emit 635 nm light. A layer of PEDOT:PSS, an organic polymer that has been proven to improve hole transport in OLEDs [7], serves as a hole injection layer. PEDOT:PSS also provides a more suitable surface energy for MEH-PPV, which promotes surface wetting to reduce pinhole formation, which helps to reduce the likelihood of device shorts. Indium tin oxide (ITO) serves as the electrodes on both sides of this structure, which is on a polyethylene terephthalate (PET) substrate. The PET and ITO are both visibly clear, allowing light to easily pass through.

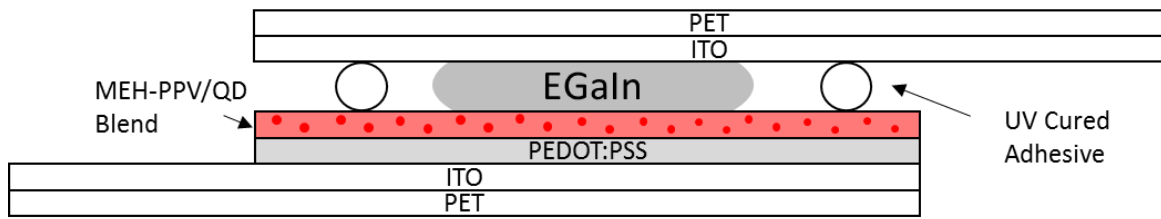


Fig. 1: Device Schematic

2 FABRICATION METHODS

2.1 Materials and Solution preparation

Flexible sheets of ITO on PET, available from Sigma Aldrich (749745), are used for the substrate and electrodes. The sheets come with a protective cover over the ITO, so minimal cleaning/preparation is required.

The hole injection layer is a solution of PEDOT:PSS in water (1.3% wt), which is available from Sigma Aldrich (483095). The organic polymer MEH-PPV (Sigma-Aldrich 753793-5ML) is prepared in a toluene solution stirred, overnight at 50 deg C. This is then combined with a solution of alloyed CdSe/ZnS, 630 nm quantum dots in toluene, 1 mg/ml (Sigma-Aldrich 753793) to create a toluene solution blend with a 1:1 PPV:QDs weight ratio of, which is again stirred overnight at 50 deg C. Gallium-Indium Eutectic (EGaIn) (Sigma-Aldrich 495425) and light curing adhesive (McMaster-Carr 74545A24) are additional materials used to secure the top electrode to the device.

2.2 Fabrication Steps

Two different devices were made – one with a MEH-PPV/QD blend active layer, and one with just MEH-PPV. Starting with a 3x6 cm sheet of PET coated with ITO, a small piece of clear tape is set to cover about 2x3 cm area at the end of the strip, as a mask. 3 or 4 drops of PEDOT:PSS solution are spin coated on at 2000rpm for 40 seconds, then dried at 80 deg C for 3 minutes, resulting in a circle of ~3 cm diameter. A second layer of PEDOT:PSS is then spun and dried using the same methods. Two layers of either the PPV-QD blend solution, or just the PPV solution, are then spun on, both at 2000

rpm for 40 seconds followed by drying at 80 deg C for 3 minutes. Before and after all drying steps, the clear tape “mask” was respectively removed and then replaced with a clean mask.



Fig. 2: ITO coated PET with transparent tape mask (left), deposited layer of PEDOT:PSS (center), Layout for EGaln and UV adhesive (right)

A UV curing adhesive is used to secure the top electrode. EGaln is implemented at the same time to provide a conductive contact between the electrode and polymer layer. A small droplet of Ga-In eutectic is applied to the center of the coated area, and a ring of UV cured adhesive is applied, with the Ga-In at the center. A second 3x6 cm sheet of ITO covered PET is then placed on top. This is placed to keep the 2x3 cm area of ITO that was covered by the mask during spin coating exposed, while completely covering the GaIn eutectic and the adhesive. The layout of this architecture can be seen in fig. 1. This alignment allows for the two exposed ITO tabs at opposite ends of the device to serve as connecting electrodes. The device is then set under ultraviolet light for 60 seconds to cure the adhesive.

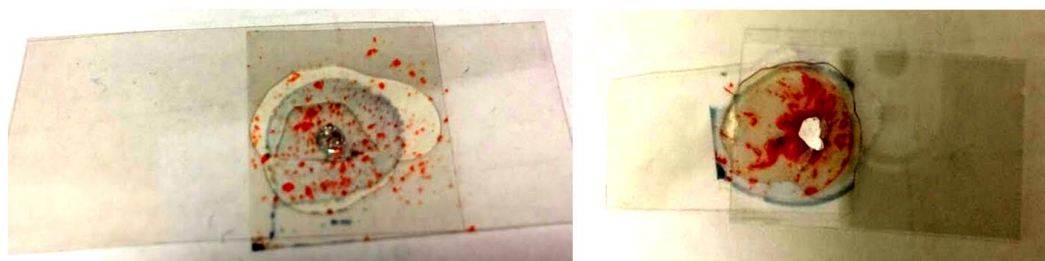


Fig. 3: Finished devices using a MEH-PPV/QD blend (left) and MEH-PPV (right) as functional layers

3 EVALUATION

Checking the device resistance is a quick way to determine if it will function properly before connecting it to power. If the resistance is in the 1-5 k Ω range, there is a short in the device, meaning it will not function properly. If the resistance is orders of magnitude higher than this, it is worth applying power to see if light is emitted.

The device was connected to a DC power source, and light is visible once 9V of power is applied. To determine if the QDs contributed to emission, light spectrum analysis was applied with a Horiba iHR550 spectrometer for both devices with and without QDs, with 14V of applied power. A CMOS camera was used to collect images of the illuminated device, and spectroscopy analysis was performed with a Horiba iHR550 imaging spectrometer. CMOS camera images show that small, discrete areas are illuminated on both devices. Spectroscopy shows a noticeable difference in both the power and wavelength of lights emitted between the two samples.

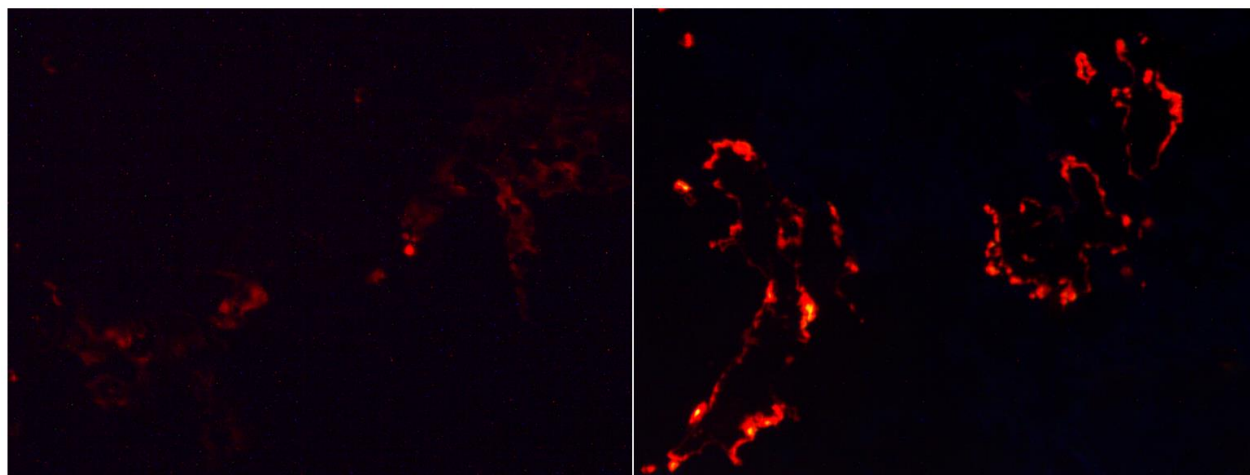


Fig. 4: CMOS PL images of MEH-PPV (Left) and MEH-PPV/QD Blend (Right)

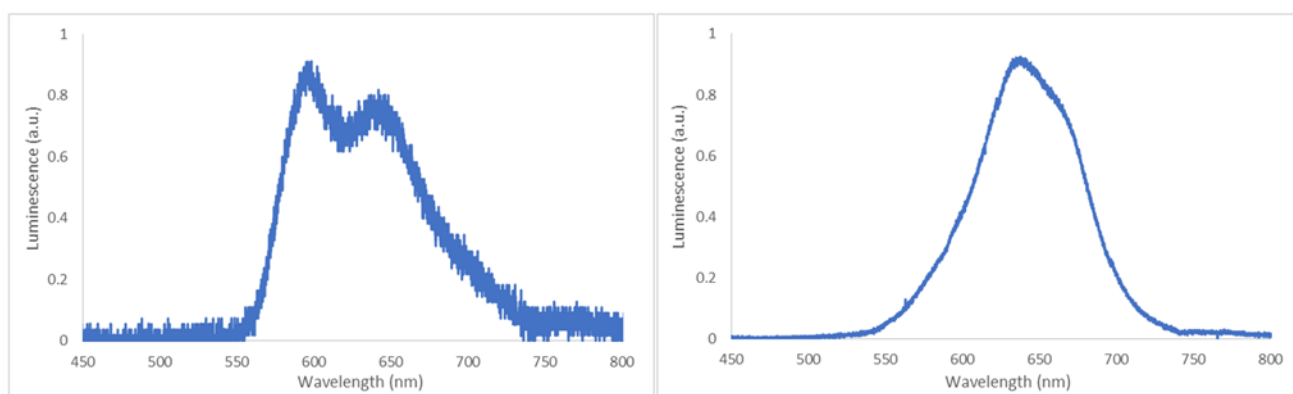


Fig. 5: EL Spectra of MEH-PPV (Left) and MEH-PPV/QD Blend (Right)

4 RESULTS AND DISCUSSION

4.1 Electroluminescence

Results from the camera images show that the current methods do not produce discrete, inconsistent areas of light emission. In theory, any area of MEH-PPV in contact with the Ga-In eutectic should emit light. The presence of any light emission signifies that there is no electrical short within the device, but the inconsistencies must be a result of something within the device structure, either in the active element, or in the conducting layers. From the areas that do emit light, spectroscopy results show two peaks from the MEH-PPV, at ~ 598 nm and ~ 641 nm, and a single peak from the MEH-PPV/QD blend at ~ 637 nm. This peak matches the wavelength of the QDs used, providing evidence that the QDs are contributing to light emission. Both the images and spectroscopy show that the PPV-QD sample provided overall higher emission, but this was true across all wavelengths, suggesting it was not a result of the QDs. Both the emission power differences and discrete emission areas are likely due to inconsistencies created from the fabrication process.

Similar fabrication methods have previously been proven to work, with more consistent emission areas, on glass substrates. The authors recognize two possible reasons for the inconsistencies seen in this work— the sandwiching technique using eutectic and adhesive, or the MEH-PPV deposition methods. These are seen as the two main contributions to the shortcomings of the fabricated devices.

External quantum efficiency (EQE) is one of the most important characteristics for evaluation of polymer light emitting diodes. Typically, measurements of the entire light spectrum from an integrating sphere are required to determine the EQE of a light emitting device. More recently, methods have been developed that provide an accurate estimate of EQE from measurements made from simpler, more affordable measurement systems [14], such as the Hiroba device used to observe the emission spectrum in this work. While these methods could provide an EQE estimate, a limited area was observed for measurements, and within that, only a limited area was actively emitting light. Because of these conditions, the data collected can be used to observe the emitted spectrum, but may not be suitable for EQE characterization. Images of the devices show that the red-orange MEH-PPV areas are not distributed very evenly, suggesting that improvements to the polymer deposition process could result in more consistent emission areas.

5.2 Photovoltaics

An attempt to observe a photovoltaic effect from the fabricated devices was made, but there was no noticeable difference between measured dark and photocurrents. Photovoltaic devices with similar structures, including a hybrid organic/inorganic functional layer, have been reported [15, 16]. This suggests that a photovoltaic effect may be present in the devices fabricated in this work, but cannot currently be observed. We present three possible factors that may contribute to this issue; the hole injection layer, the electrode material, and the deposition methods used.

PEDOT:PSS was chosen as a polymer electrode to promote better device EQE. By acting as a hole injection layer, it helps to lower the injection barrier that is often seen at an interface between a metal electrode and an organic polymer, like MEH-PPV [7]. Prominent work in this area uses another polymer, poly (p-phenylenevinylene) (PPV), in the same position – between the ITO anode, and the polymer/QD blend [15]. The PPV was reported to actually lower device efficiency, but help improve the photovoltaic effect by lowering the device's overall dark current, which makes the photocurrent easier to measure. PPV is reported to lower the dark current by introducing an injection barrier between the ITO and the functional layer. The fact that PEDOT:PSS lowers the injection barrier at the same interface suggests that it increases the dark current in this work's device, which may be why it is difficult to observe a photovoltaic effect. Similar work has reported a measurable photovoltaic effect with the use of PEDOT:PSS as a hole injection layer, suggesting that this may not be the prominent reason that it could not be observed in this work [16].

Simplified fabrication techniques resulted in ITO being used for both electrodes in this device. Similar work commonly uses ITO and another metal Al or Mg, which results in a work-function difference between the two electrodes. This difference results in "band tilting", which is reported to further increase the energy barrier created by PPV, which lowers dark current [15]. When both electrodes are ITO, this tilting effect will not occur. This work does use EGaIn, which is reported to have similar work-functions to Al [17], which may be considered as the second electrode. With this respect, the work-functions of this device with an ITO/PEDOT:PSS and EGaIn/PEDOT:PSS electrodes may be similar to that of a reported photovoltaic device with ITO/PEDOT:PSS and Al electrodes, which did report performance limitations from dark currents [16]. Better photocurrents are reported from a device that uses ITO and Mg as electrodes, which have a greater work-function difference and thus provide more band-tilting. Deposition of both Al and Mg are typically done through thermal evaporation – Mg in particular requiring an inert environment for safe use. This additional step requires more complicated equipment than that used in this work, but does have the potential to provide overall better, more reliable performance.

The fabrication approach and substrate chosen for this work also present performance limitations that cannot be ignored. Similar work spin coating light emitting polymers on glass substrates include annealing the polymer at 200 deg C [16]. Because of the low glass transition temperature of the flexible PET used in this work, baking at such temperatures was not a possibility, but exploring how this effects performance could be worthwhile. More prominent work performs deposition steps under

vacuum [15, 7], which will help reduce structure imperfections from contamination when compared to deposition at atmosphere. As an example, spinning and baking a layer of PEDOT:PSS in atmosphere, as was done in this work, is reported to cause etching into the ITO layer, which can reduce overall device efficiencies [18]. The inconsistent emission areas and inability to observe a photovoltaic effect in this work may be a result of the level of control lost from the simplified fabrication steps used. Interestingly enough, similar work seems to rely on this property of MEH-PPV, using it in a blend with another polymer to create small MEH-PPV pixels in the functional layer [19]. This may suggest that other polymers, or a polymer blend could be explored for better results using simplified fabrication.

5 CONCLUSIONS

This work has shown how simplified methods can be used to create a light emitting device with quantum dots, but also shows the potential limitations of the methods chosen. The work presented has proven that these methods can successfully create an optoelectronic device from a Polymer-QD blend on a flexible substrate. The discrete emissive areas, as well as missing evidence of a photovoltaic effect serve as proof of challenges that are yet to be overcome with the current methods. More sophisticated fabrication steps would allow improvements to be made through control of energy alignment from more available electrode materials, and a cleaner, more controlled process through deposition done through better equipment systems. With the motivation of low cost, flexible optoelectronic devices, it would be worthwhile to track device improvements from single improvements to the fabrication process, with the goal of achieving a balance between performance and fabrication simplicity. The first attempt at improvement would be to remove the sandwich-style architecture by replacing the second ITO coated PET layer, which required the eutectic and adhesive, with a metal electrode that can be thermally evaporated directly onto the functional organic substrate. The eutectic-adhesive sandwiching technique has worked on solid glass substrates, but this work shows that it is not ideal for use on flexible substrates, as it eliminated the ability for flexibility analysis. The cured adhesive has proven to be quite inflexible, and thus renders the devices rather fragile. Introduction of this process would reduce fabrication simplicity, but help improve device flexibility, as well as improve optoelectronic performance. After observing how a metal electrode changes device performance, changes can be made to the MEH-PPV layer for further improvements. The work presented sets a foundation for simplified fabrication techniques for flexible optoelectronic devices, and sets a clear path for improvements.

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