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Stackable spectral-sensitive conductive films based on cyanine aggregates *via* an inkjet method

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ABSTRACT

In this work, wavelength sensitive organic bulk-hetero photodiodes were fabricated by a piezoelectric inkjet method based on the J-type aggregates of cyanine dye molecules doped into poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) thin films on indium tin oxide anodes. The cyanine dye concentration in the inkjet printed films was optimized and the J-aggregate formation during the drying process was investigated by local absorption spectra. It was found that at lower dye concentrations, not only the J-aggregate formation but also the radiation sensitivities of the films were improved significantly. Moreover, the stacking of the cyanine dye – poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) spots demonstrated the linear increase on the optical density and film thickness without deteriorating the J-aggregate formation, indicating their potential in application as narrow band filters.

1. Introduction

Over the last few years, inkjet printing has attracted extensive research interest as a direct patterning technique for the cost-effective fabrication of organic optoelectronic devices such as organic light-emitting diodes (OLEDs) [1–4], organic field-effect transistors (OFETs) [5–7], organic solar cells (OSCs) [8–10], and microstructures and tracks, etc [11–15]. In comparison with other film deposition techniques for organic chemicals, the inkjet method was highly preferable owing to its versatility, miniaturization, and high-precision patterning. Inkjet printing especially the drop-on-demand (DoD) had the advantages such as being fast and simple with high throughput. The consumption of materials could be reduced to an extremely low level, pico liter of each droplet in volume, providing a low cost, mask free, and non-contact printing approach [1]. It was suggested that DoD inkjet printing might be one of the most suitable technical pathways for the fabrication of integratable and miniaturized optoelectronic elements, e.g. photodiodes and narrow band filters on disposable micro-flow cytometry chips [16,17]. The other techniques such as spin-coating or dip-coating were not applicable on these occasions because of the complicated structures of the flow cytometry chips, risk of contamination, and infeasibility to integrate various functional elements on one single chip. In this concern, organic photodiodes in the visible region were recently developed by the piezoelectric inkjet printing technique by our group for the first time, which demonstrated the resolving capability on incident wavelength or energy [17–20].

As the active materials for photodiodes which were capable of spectral resolving, J-type aggregates of cyanine dyes were adopted. Due to the hydrophobic character of their molecular frames, cyanine dyes tended to form self-aggregates in aqueous solutions, which have wide applications [21] and could be classified into J- or H-type aggregates, with an intense red-shifted or broad hypsochemically shifted absorption spectrum respectively, in

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comparison with the monomer counterparts, depending on the angle between the transition dipoles and molecular axis of the aggregate [22,23].

In our previous reports, an inkjet fabrication method on the J-aggregated cyanine dye doped conductive polymer films has been introduced, followed by the development of a disposable and printable organic bulk-hetero junction photodiodes, which showed spectral resolving capabilities at the absorption peak of each cyanine dye, due to the narrow band absorption of the J-aggregates [19,20]. However, some crucial problems remain pending. For instance, as key parameters of these organic photodiodes, the spectral resolution and sensitivity were low, which were suggested to be ascribed to the unoptimized J-aggregate formation during the printing process. Because of the restriction on solution viscosity for stable droplets ejection, which was mainly decided by the dye and polymer concentrations, the average film thickness was normally less than 40 nm, which limited the optical density of the film to be less than 0.7 at the absorption peak. Thus, the composition ratio of the cyanine dye to the conductive polymer was constrained to be high in our previous reports so as to keep the optical density at a practical level [19,20]. The unoptimized cyanine dye concentration and as a result, the poor J-aggregate formation and limited optical density might be partially responsible for the low sensitivity and spectral resolution of the organic bulk-hetero photodiodes and also impeded their other applications, for instance, as the narrow band optical filters.

In this work, the dependence of J-aggregate formation on the cyanine dye concentration in inkjet printed films was investigated by the macroscopic and local absorption spectra, respectively. It was found that the spectral-resolving capability and radiative sensitivity in name of quantum efficiency of organic bulk-hetero photodiodes at lower cyanine dye concentration were improved significantly due to the better J-aggregate formation and depression on fibril structures. Moreover, the optical density of the films could be tailored linearly by stacking of layers vertically while the J-aggregate formation was retained, indicating that stackable inkjet fabrication as a promising method for disposable miniaturized optical elements, e.g. narrow band filters in the visible region.

2. Experimental section

The cyanine dye, 5-phenyl-2-(2-{[5-phenyl-3-(3-sulfopropyl)-2-(3H)-benzoxazolylidene]methyl}-l-butenyl)-3-(3-sulfopropyl) benzoxazolium hydroxide, inner salt, compound with triethylamine (NK-1952, Hayashibara Biochemical Lab.) and poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, Sigma–Aldrich, 0.175 wt% in H_2O solution) were used as received without further purification. The chemical structures of NK-1952 and PEDOT:PSS were shown in Fig. 1. Firstly, the NK-1952/PEDOT:PSS solution was made by mixing the cyanine dye with PEDOT:PSS in aqueous solution with the deionized water containing a trace of surfactant (Triton-X). The dye/polymer ratio was kept at 2.5:1, 5:1, 7.5:1, and 10:1 in weight, respectively. After vigorous stirring followed by the ultrasonic treatment to complete the dissolution of the dye, the viscous NK-1952/PEDOT:PSS solutions were filtered (Whatman filter GF/B 1.0 μm) before use.

A piezoelectric inkjet system (Microjet IJK-200s) with a nozzle size of 70 μm in inner diameter was used with the indium tin oxide (ITO) coated polyethylene terephthalate (PET) films as the substrates. In this work, the inkjet conditions such as pulse voltage and pulse duration were fixed at 75 V and 67 μs, respectively. UV exposure (172 nm, 10 mW/cm^2, Ushio UER20-172) was applied to the ITO substrates before printing as the hydrophilic treatment. Films in any patterns could be made by overlapping neighboring spots by a negligible degree. To avoid the environmental turbulence

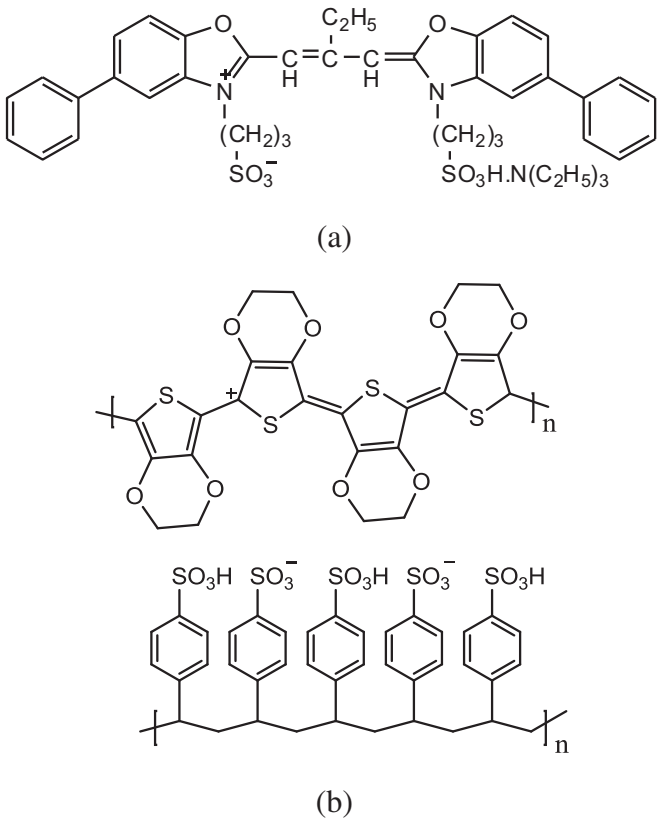

Fig. 1. Chemical structures of NK-1952 (a), and PEDOT:PSS (b).

interference on the droplet, the distance between the jet nozzle and the substrate was less than 1 mm. The macroscopic absorption spectra of the large area films (9 × 9 mm) were measured by an absorption spectrometer (Shimadzu, UV-160A). The microscopic images and local absorption spectra of various sites of the inkjet printed spots were evaluated with an optical microscope (Nikon, Eclipse TE2000U) and a multiple channel spectrometer (Ocean Optics, USB2000). The morphology of the inkjet printed NK-1952/PEDOT:PSS spots were measured by atomic force microscopy (AFM; Keyence VN-8000M/8010M).

To make the organic bulk-hetero photodiodes, the ITO substrates were etched by 10% of aqua regia (20 s) with masks to obtain designed patterns before the UV exposure and inkjet printing. Small area films of NK-1952/PEDOT:PSS in the size of 1 × 1 mm, consisting of ~46 overlapped spots were printed onto the ITO patterns as the bulk-hetero layers. After inkjet printing, a thin Al layer was vapor deposited (ULAC,VPC-410, 6×10^{-3} Pa) on the top of cyanine dye films as the cathode while the ITO behaved as the anode, and thus the bulk heterojunction photodiodes were made. The open-circuit voltage (Voc) between the cathode and anode of the inkjet printed organic bulk-hetero photodiodes was measured by oscilloscope (Tektronix, TDS 3032) under the excitation of a passively Q-switched and frequency-doubled Nd:YAG laser (0.5 ns, 532 nm). The laser beam was injected from the ITO side of the organic photodiodes at the maximum energy and repetition rate of 26 μJ/pulse and 500 Hz, respectively.

3. Results and discussion

At the fixed inkjet conditions and PEDO:PSS concentration, the effect of the cyanine dye concentration on J-aggregate formation in inkjet printed films was investigated, as shown in Fig. 2. In all