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Study on Preparation of Organometal Halide Perovskite and Electron-transporting Layer Thin Film by Ink-jet Printing

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Abstract

In this study, we report to prepare two-dimensional perovskite organometal halide and electron-transporting layer thin films, which are the key layers of solar cell devices by ink-jet printing method. We have developed controllable and optimal inkjet printing process for the growth of perovskite organic metal halide and electron-transporting layer thin films by varying solution properties, printing process parameters (e.g. droplet diameter, voltage, droplet spacing, printing pass), as well as substrate temperature, etc. This demonstration of preparation for organometal halide perovskite and electron-transporting layer films though ink-jet printing offers scope for applying printed electronics technology to manufacture optoelectronic devices.

Keywords

Organometal halide perovskite; Ink-jet printing; Electron-transporting layer ;Thin film.

1. Introduction

Organometal halide perovskite [1] has recently emerged as a highly promising excellent photoelectric functional material, which renders great potential applications in photovoltaics, light emitting diodes, photodetectors [2-4]. Organometal halide perovskite material based solar cells combine the advantages of low cost, high conversion efficiencies and simple fabricating process, establishing foundation for the possibility of commercialization [5],which have led to power conversion efficiencies over 20 per cent. However, their environmental stability for photovoltaics and other optoelectronic applications is poor. Recently, It is reported to solve the problem that Hsinhan Tsai[6] et al. have reported that the layered perovskites Ruddlesden–Popper perovskites have shown great potentials for the applications in perovskite solar cells due to their better environmental stability by producing thin films of near-single-crystalline quality, in which the crystallographic planes of the inorganic perovskite component have a strongly preferential out-of-plane alignment with respect to the contacts in planar solar cells to facilitate efficient charge transport. Therefore, photovoltaic efficiency of 12.52 per cent and greatly improved stability compared to three-dimensional perovskite materials[6].

The properties of perovskite film significantly influence the performance of the solar cell devices. Preparation of organometal halide perovskite thin film usually by spin-coating method, has the following deficiency, such as difficult to control the morphology, thickness and shape of film, pollution caused by waste of materials, low-efficient manufacturing, unable to achieve large area fabrication, etc. Ink-jet printing technology [7-10]has developed rapidly for its promising application in coatings with thin polymer films, the fabrication of solar cells [11], etc. Ink-jet printing technology relies on thermal, electro-spinning or piezoelectric injection of ink drops on the substrates [12].

This study on preparation for organometal halide perovskite layers though ink-jet printing offers scope for developing printed electronics technology to manufacture organic or organic/inorganic hybrid structures that combine the advantages of low cost (large area) and fast process (high efficiency) for potential applications in optoelectronic devices.

2. Experiments

In this study, we have synthesized such two-dimensional organometal halide perovskite as $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$(n=1~50) ($BA=C_4H_9NH_3$, $MA=CH_3NH_3$) through one-step method. The Ruddlesden–Popper layered perovskites used in this study was $(BA)_2MA_{49}Pb_{50}I_{151}$, which was dissolved in the solvent of DMF and DMSO.

Here electron-transporting layer films for solar cell devices fabricated by ink-jet printing method have been also investigated. Water-dispersed SnO_2 hydrosol has been prepared into stable dispersion as an ink.

The viscosity of the solution is relatively low, which is suitable for printing. The coatings of the perovskites and SnO_2 hydrosol were performed on ITO glass substrates by a Dimatix Materials Printer (DMP2800) .Before printing, ITO coated glass substrates have been cleaned by ultrasonication in acetone, ethanol and deionized water in turn for 15 min and heated at 150 °C for 5 min.

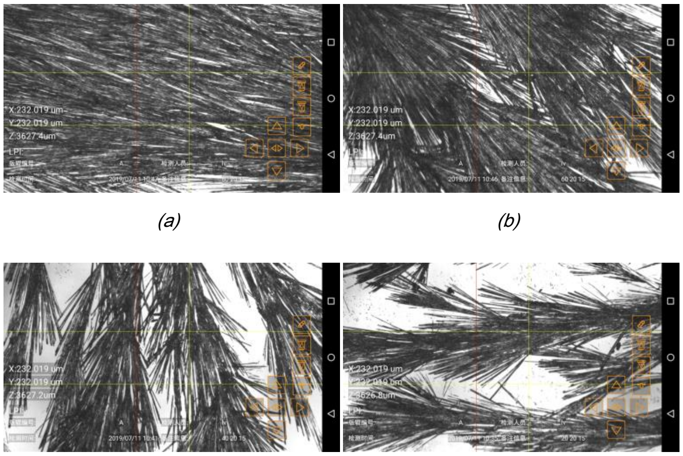
By controlling the printing process parameters (e.g. printing voltage, droplet spacing, printing pass), we are able to provide with the optimized inkjet printing process for fabrication of organometal halide perovskite thin film and electron-transporting layer (SnO_2). Here we varied the printing parameters with 20-80 μm droplet diameter, 5-20 μm droplet spacing, 5-25V nozzle voltage, 1 to 3 printing passes. Though the ink-jet printing process, we have obtained the optimum conditions for perovskite and electron-transporting layer (SnO_2) thin film.

The surface morphology of thin films prepared by different printing process has been characterized by ReDot-PRO (a portable three-dimensional image-capturer), as well as the photo-luminescence property of perovskites.

Photoluminescence spectra of the perovskite film were measured by Fluorescence Spectrophotometer(F-4600).

3. Results and Discussion

During ink-jet printing process, different printing parameters were varied to obtain better quality films. Fig.1 showed the magnified image of the printed perovskite films.



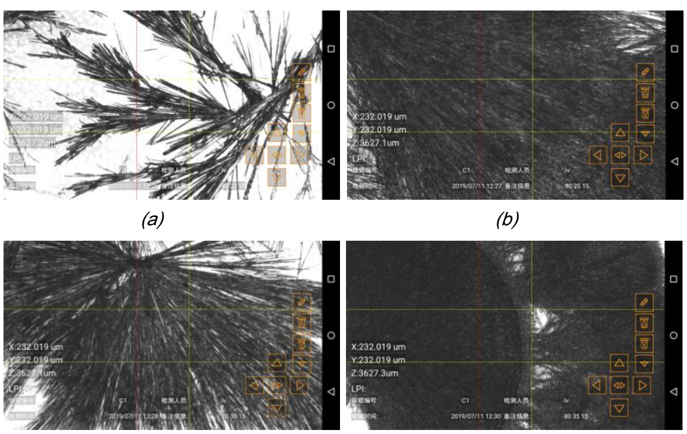
(a) (b)

(c) (d)

Fig.1 inkjet-printed films under the same printing condition except varied droplet diameter as (a) 80μm, (b) 60μm, (c) 40μm, (d) 20μm

The optimum conditions for inkjet printing were found that the droplet diameter was 80μm, while the voltage was 25V and the droplet spacing was 15μm.

As seen from the Fig.1,droplet diameter had a great effect on to the uniformity of the films in inkjet printing. When the diameters increased, the spreadability would be better and the highly crystalline film became more uniform. The film seems uniform and highly crystalline always indicating that it is ideal for fabrication of solar cell devices.



(a) (b)

(c) (d)

Fig.2 Inkjet-printed Fig.1 inkjet-printed perovskite films under the same printing condition except varied voltage as (a) 22V, (b) 25V, (c) 30V, (d) 35V

Fig.2 showed the morphologies of different perovskite films by controlling the nozzle voltage in the ink-jet printing process. As seen from the Fig.2, the optimum conditions for inkjet printing were found that the voltage was 25V, the droplet diameter was 80μm and the droplet spacing was 15μm. It was indicated that nozzle voltage can also affect the uniformity and spreadability of the films during inkjet printing process. When the nozzle voltage was 25V, it achieved the best spreadability and uniformity. As the voltage decreased below 25V, the grains aggregated. However, when the voltage increased above 25V, the film became inhomogeneous.

The photoluminescence spectra of the perovskite films using Fluorescence Spectrophotometer F-4600 are illustrated in Fig.3. It can be observed that the peak at 1.64 ev indicated the emission of $(BA)_2MA_{49}Pb_{50}I_{151}$.

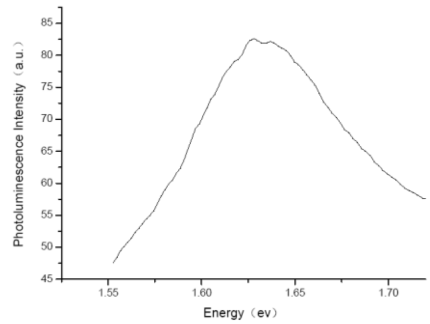
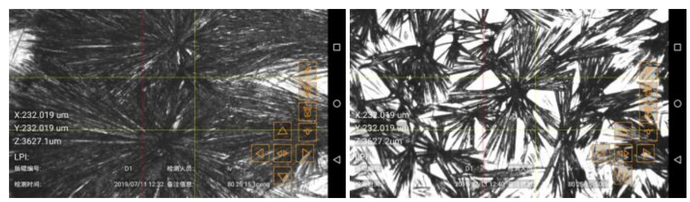


Fig.3 Photoluminescence spectra of the perovskite film



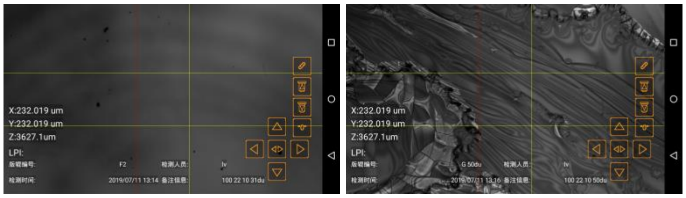
The temperature of the substrate was varied from room temperature to 50 °C, as illustrated in the images shown in Fig.3

(a) (b)

Fig.4 Inkjet-printed perovskite films under the same printing condition except the varied substrate temperature as (a) room temperature, (b) 50°C

As shown in the Fig.4, the needlelike grains aggregated markedly as the substrate temperature increases from room temperature up to 50°C.It caused less uniformity and coverage of the coating.

Electron-transporting layer films for solar cell devices have been fabricated by ink-jet printing method in this study. We also varied the printing parameters with droplet diameter, droplet spacing, printing voltage, printing passes to obtain SnO_2 coatings with good quality. The optimum conditions for inkjet printing were found that the voltage was 22V, the droplet diameter was 100μm and the droplet spacing was 10μm. The morphology of electron-transporting layer films fabricated by ink-jet printing method had been shown as Fig.5:



(a) (b)

Fig.5 Inkjet-printed SnO2 films under the same printing condition except the varied substrate temperature as (a) room temperature, (b) 50°C.

As seen from the images, smooth and uniform films of SnO2 have been prepared through ink-jet printing process at room temperature. When the substrate temperature increases from room temperature up to 50°C, it also caused less uniformity of the SnO_2 coating. Multi-pass printing is usually used to improve uniformity and increase thickness. In this study, we printed perovskite layer onto SnO2 coating, illustrated as Fig.6. It can be observed the surface coatings are uniform and highly crystalline.

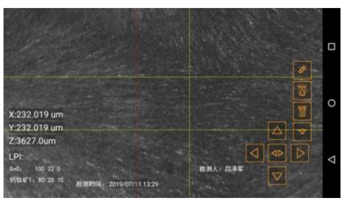


Fig.6 Multi-layered film of perovskite onto SnO2 by ink-jet printing

4. Conclusion

In summary, well-dispersed printable inks of two-dimensional perovskite organic metal halide and water-dispersed SnO2 hydrosol were prepared for the ink-jet printing process. The controllable and optimal inkjet printing process for the growth of two-dimensional perovskite organic metal halide thin film and electron-transporting layer film have been obtained from this study, by controlling the printing process parameters (e.g. voltage, droplet diameter, droplet spacing, printing pass, substrate temperature). It will offer a possible fabrication route to manufacture organic or organic/inorganic hybrid structures for potential applications in optoelectronic devices.

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Yingqun Qi holds a Ph.D. degree of Physical Chemistry from Technical Institute of Physics and Chemistry, Chinese Academy of Sciences. Her major research interests include conducting polymers, organic/inorganic hybrid, 3D printing, printable materials, etc. She has been principal investigators and co-principal investigators for a number of provincial and ministerial funding projects and published over 10 academic papers in related research areas.

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