

## Supporting Information

### Grain Size Control for High-performance Formamidinium-based Perovskite Solar Cells via Suppressing Heterogenous Nucleation

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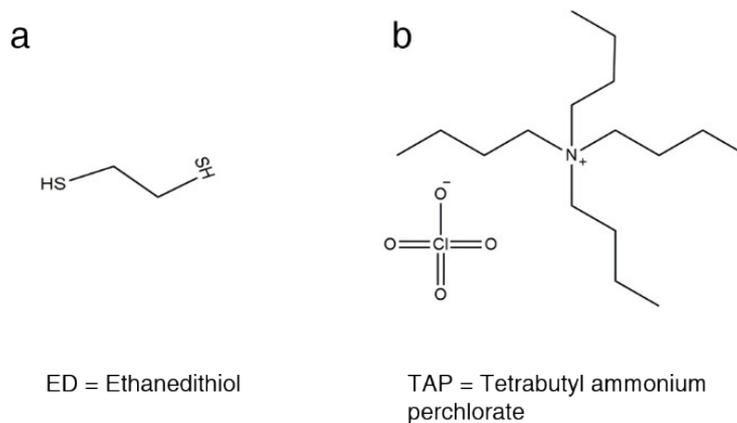
**Table S1.** Viscosity measurements of control & W/ED+TAP precursor solutions.

	Density (g/cm <sup>3</sup> )	Time (s)	Viscosity (Pa·s)
Control solution	1.294	1710	1.816
W/ED+TAP solution	1.306	1776	1.904

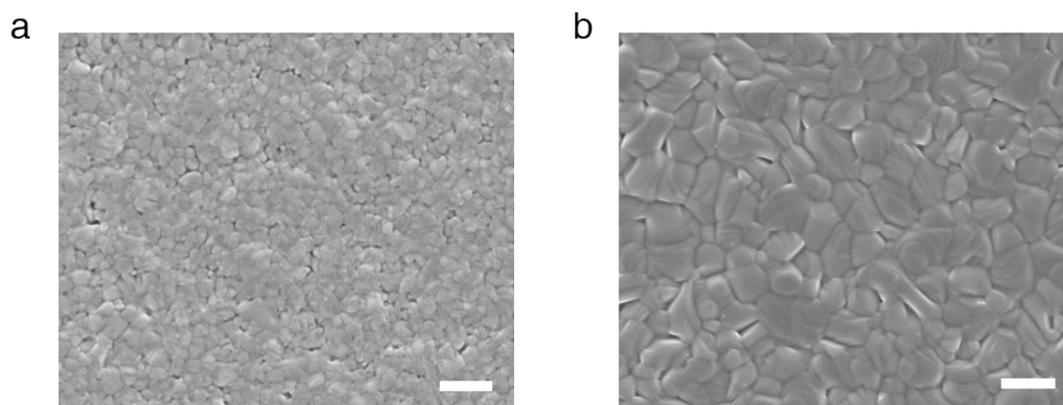
By using the formula  $\eta = A\rho T^1$ , solutions viscosities were measured with the help of Ubbelohde viscometer, where  $\eta$  is the viscosity,  $A$  is the characteristic parameter of the viscometer,  $\rho$  is the solution density, and  $T$  is the time for a certain volume of solution to flow through the capillary of the viscometer.

**Table S2.** The corresponding photovoltaics parameters of the devices based on control & W/ED+TAP perovskite films.

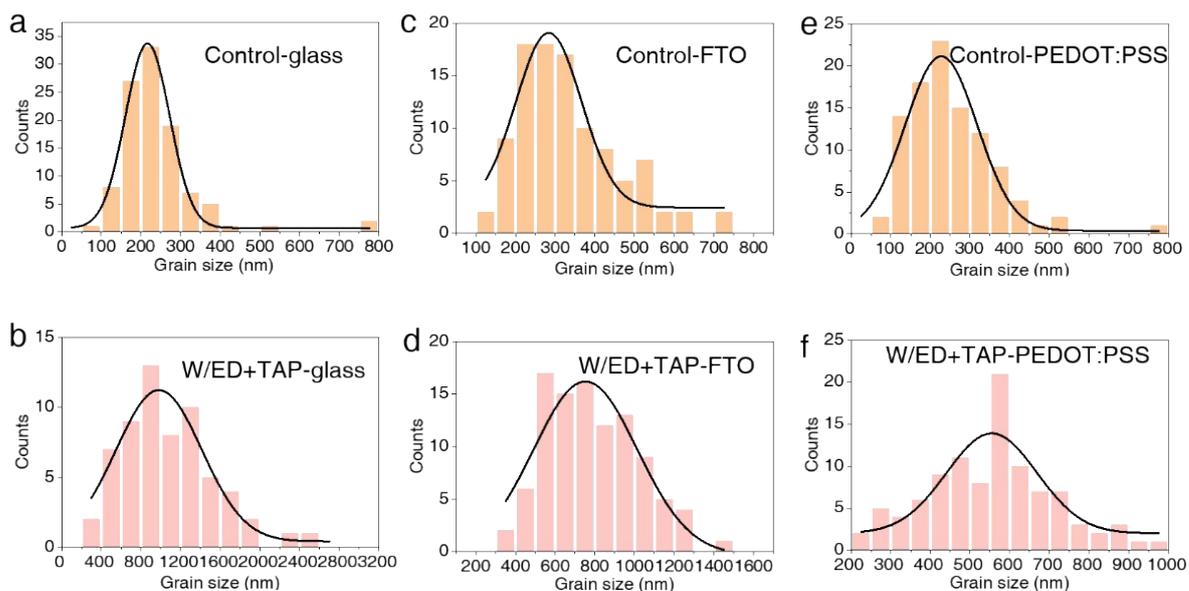
	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
Control	1.083	22.03	72.52	17.30
W/ED+TAP	1.094	23.82	77.39	20.15



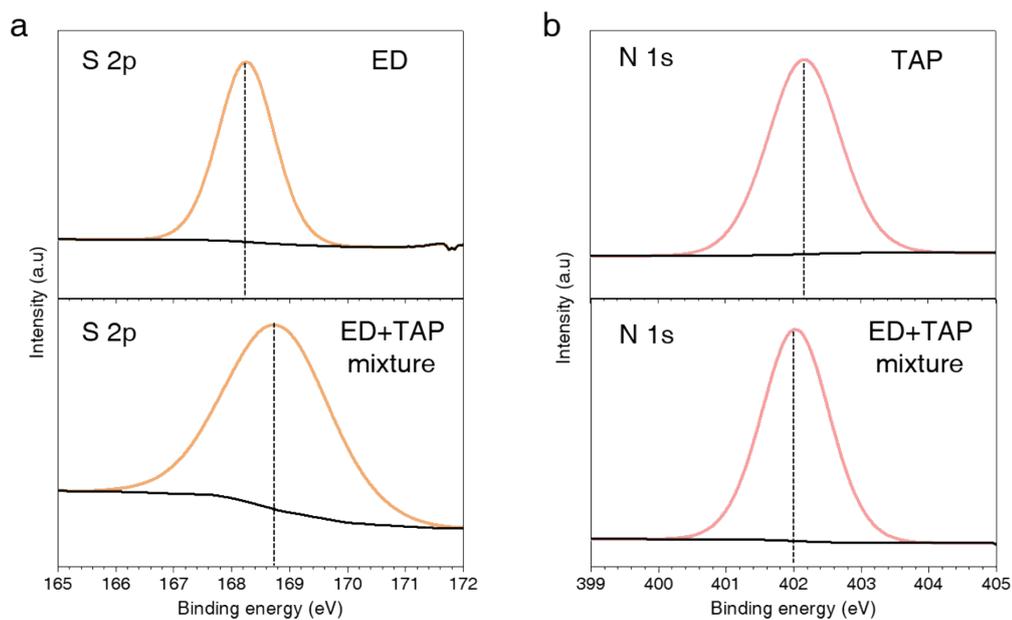
**Fig. S1** The chemical structures of the ED and TAP.



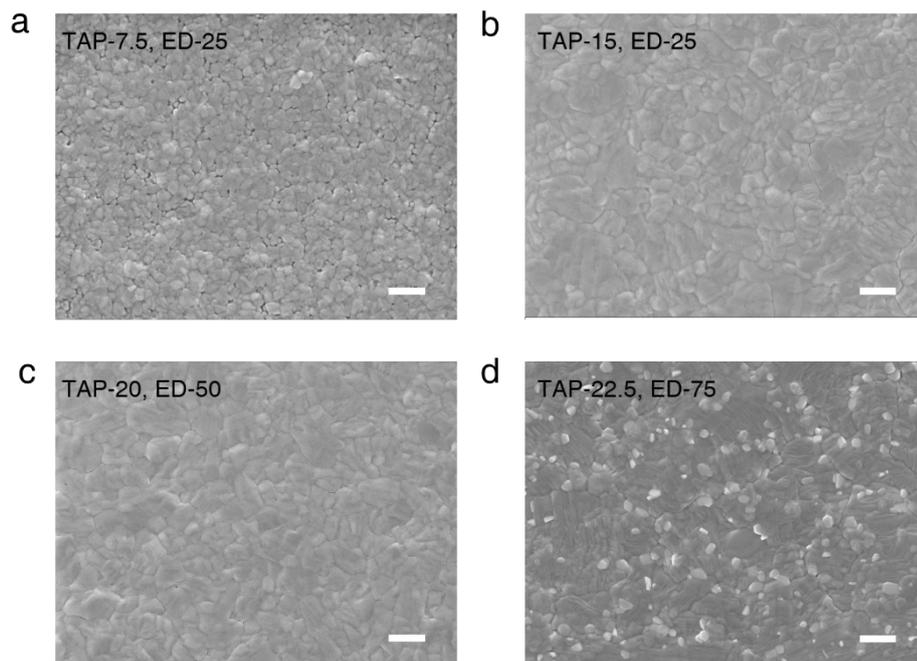
**Fig. S2** The complete SEM images of perovskite films on TiO<sub>2</sub> substrate derived from (a) control and (b) W/ED+TAP precursor solution. The scale bars are 1  $\mu$ m.



**Fig. S3** The grain size distribution for FAPbI<sub>3</sub> films derive from control and W/ED+TAP precursor solution on various substrate.

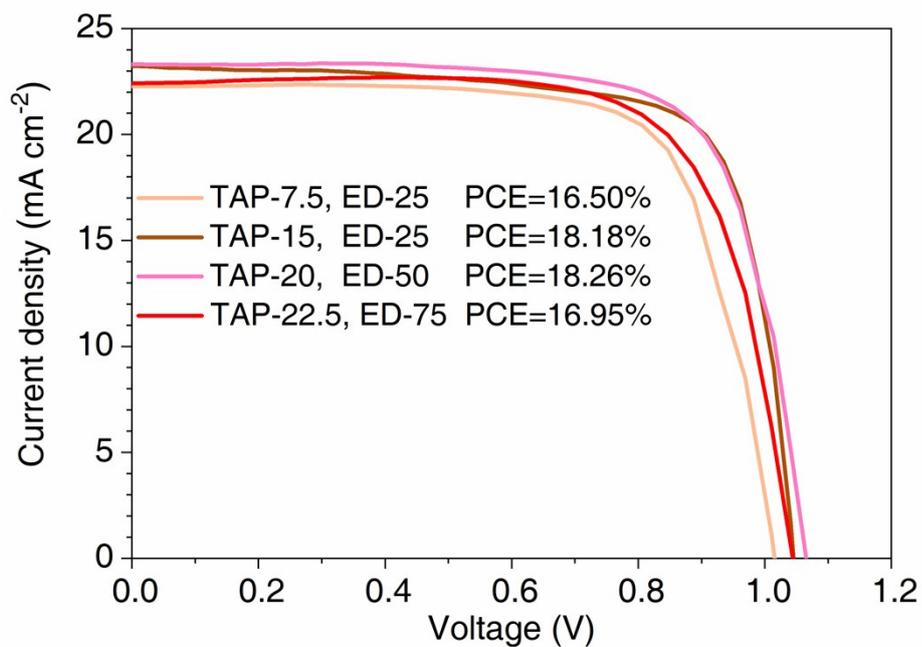


**Fig. S4** XPS spectra of (a)S 2p in ED and mixture of ED with TAP, (b)N 1s in TAP and mixture of ED with TAP.



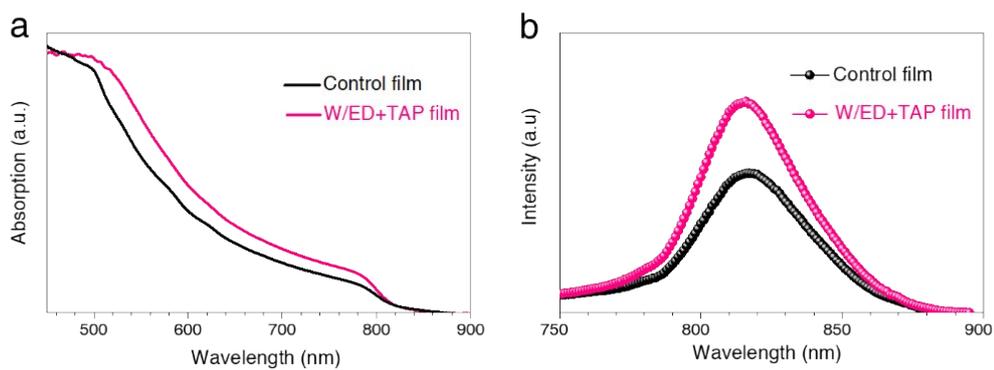
**Fig. S5** SEM images of perovskite films from precursor solution with different concentration modifiers. The scale bars are 1  $\mu\text{m}$ . TAP-7.5, ED-25 represents that 7.5 mg of TAP and 25  $\mu\text{L}$  of ED in 1 mL precursor solution.

In Fig. S5a-b, with the increase of modifiers concentration, the morphologies changed and the particle sizes increased. In Fig. S5c-d, when the concentration exceeds the optimum concentration (TAP-15, ED-50), although the particle sizes are large, the perovskite films are not smooth and uniform.

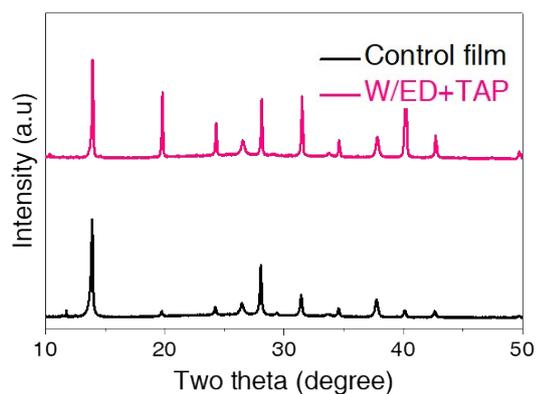


**Fig. S6** Comparisons of devices performances based on different concentration of additives.

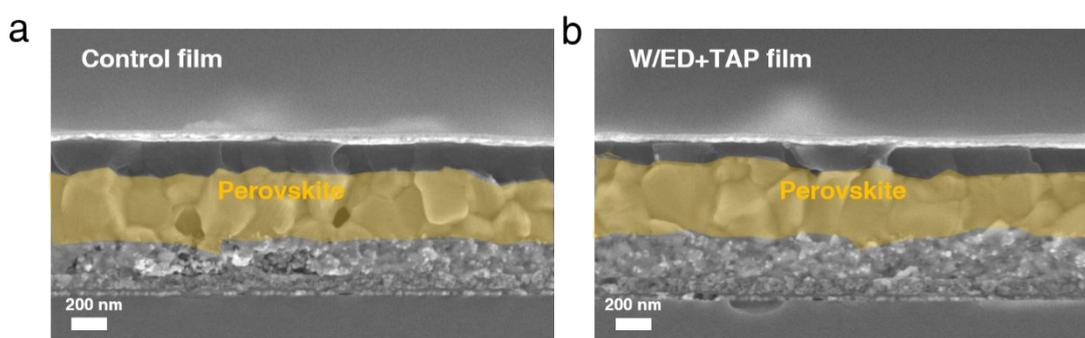
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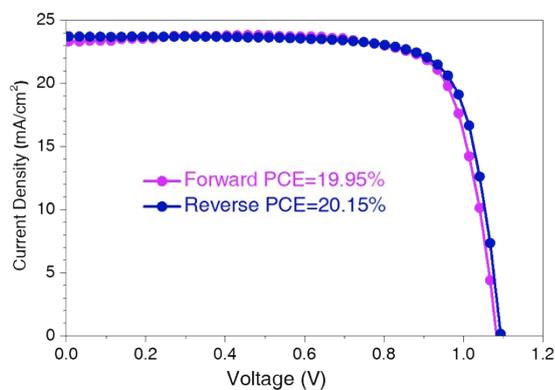
**Fig. S7** (a) UV/Vis absorption spectra, (b) PL spectra of the control and W/ED+TAP perovskite films.



**Fig. S8** XRD pattern of the control and W/ED+TAP perovskite films.

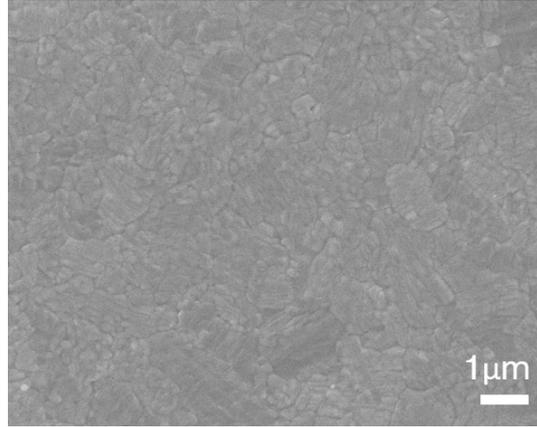


**Fig. S9** Cross-sectional SEM images of the (a) control and (b) W/ED+TAP perovskite films.



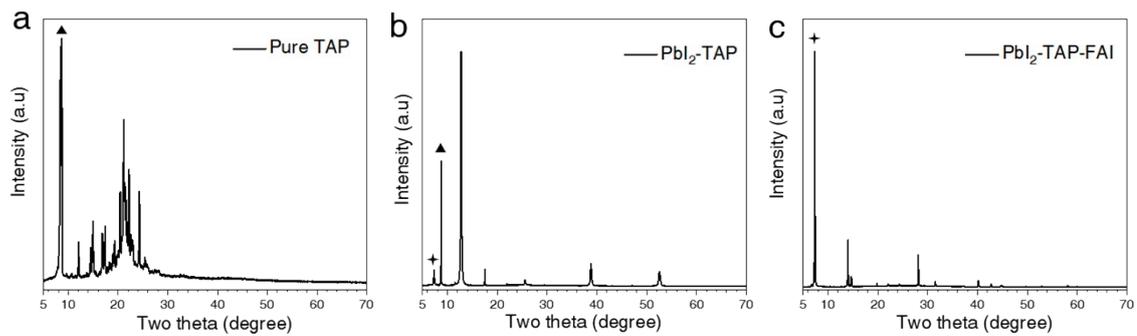
**Fig. S10** The I-V curves with both reverse and forward scans of the ED+TAP perovskite solar cell with optimal concentration of additives.

The best device exhibits a PCE of 19.95%, with a  $J_{SC}$  of  $23.50 \text{ mA cm}^{-2}$ , a  $V_{OC}$  of 1.083 V, and an FF of 78.32% in reverse direction. There is little detected hysteresis in the reverse direction and the forward direction.



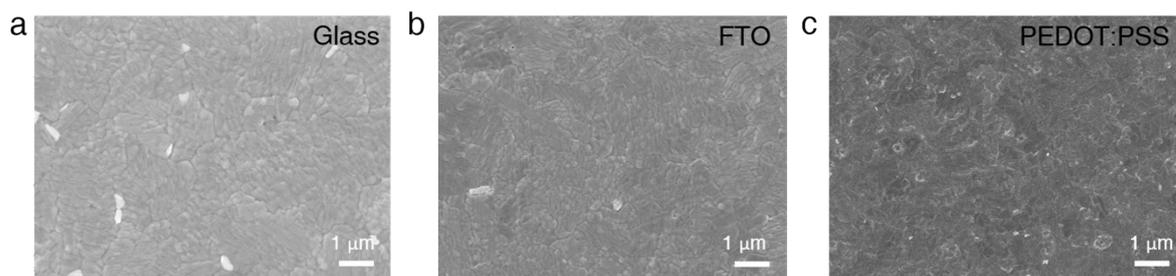
**Fig. S11** The morphology of perovskite film fabricated by the precursor solution treated by pure ED.

When we used pure ED as modifier, grain size of the film did not change significantly.



**Fig. S12** The XRD patterns of films fabricated from the pure TAP, TAP-FAI-PbI<sub>2</sub> and TAP-PbI<sub>2</sub> precursor solution.

In Fig. 12a, the peak locates at 8.8° belongs to pure TAP marked with triangular symbols. A new phase at 7.4° is formed in both Fig. 12b and c, marked with a star symbol. It is speculated that this new phase is formed by the reaction of lead iodide with TAP according to this phenomenon. In Fig. 12c, strong peak of new phase and weak peak of perovskite are observed obviously. Therefore, high quality perovskite films can not be fabricated by adding pure TAP to the precursor solution. The combination of the ED and TAP can effectively enlarge the grain size and passivate the defects due to the interaction between them.



**Fig. S13** The complete SEM images of perovskite films fabricated by control precursor solution on (a) glass, (b) FTO and (c) PEDOT:PSS substrates.

### **Experimental Section.**

#### **Solar cell fabrications.**

Fluorine-doped tin oxide (FTO) glasses (Pilkington, TEC15) were used as device substrate. FTO glass was washed by distilled water and ethanol and etched by HCl aqueous and zinc powder. The blocking  $\text{TiO}_2$  (bl- $\text{TiO}_2$ ) layer was deposited by using spray pyrolysis on the as-prepared FTO. These layers were heated at 430 °C for 30 min. In the following step, mesoporous  $\text{TiO}_2$  (mp- $\text{TiO}_2$ ) was spin-coated on the as-prepared deposited layer. The prepared films were then calcined at 510 °C for 20 min. We dissolved 206.4 mg of FAI and 545 mg of  $\text{PbI}_2$  in 800  $\mu\text{L}$  DMF and 200  $\mu\text{L}$  DMSO. This precursor solution was used to fabricate control film. We also mixed different amount of ethanedithiol (represented as ED) and tetrabutyl ammonium perchlorate (represented as TAP) in the above precursor solution. The 15 mg (0.0438 mmol) of TAP was added in the precursor solution and stirred for 1 hour. Before spin-coating, 50 $\mu\text{L}$  (0.596 mmol) of ED was mixed into the solution and stirred for 5 minutes. 50  $\mu\text{L}$  solution was spin-coated on the mp- $\text{TiO}_2$  layer at 1100 rpm for the first 10 seconds and 5000rpm for the next 40 seconds. CB was spin-coated at cutdown 30 seconds. The prepared film was then annealed at 170 °C for 20 minutes. Spiro-OMeTAD was used as hole-transportation layer. The spiro-OMeTAD solution mentioned above consisted of spiro-

OMeTAD (73 mg), 4-tert-butyl pyridine (28  $\mu\text{L}$ ) and lithium bis(tri fluoromethanesulfonyl)imide (Li-TFSI) solution (17.5  $\mu\text{L}$ ) (520 mg of Li-TFSI dissolved in 1 mL of acetonitrile) dissolved in 1 mL CB. Finally, Au electrode of 60 nm was made by vacuum thermal evaporation method.

## Characterization

The perovskite film morphology was obtained by field emission scanning electron microscope (FEI Sirion 200). The crystallinity and intensity of the perovskite layer were determined by X-ray diffractometer (XRD) (Rigaku, Smartlab, Japan). We measured the photocurrent density-voltage ( $J-V$ ) curves using a solar simulator (94042A, USA). The measurement of  $J-V$  curves were controlled under the condition of 1 sun illumination. The solar simulator was equipped with a Keithley 2420 source meter. During the measuring process, a square mask of 0.09  $\text{cm}^2$  area was used. We used this method to avoid light scattering and determine the effective area of the device. Absorption spectra was recorded on an ultraviolet-vis (UV-vis) spectrophotometer (U-3900H, HITACHI, Japan). Steady-state PL spectra were tested by a spectrofluorometer (photon technology international). The exciting wavelength was 473 nm and excited by a standard 450 W xenon CW lamp. Incident photon to current efficiency (IPCE) were collected as a function of wavelength from 300 to 900 nm (PV Measurements, Inc.), with dual Xenon/quartz halogen light source, measured in DC mode with no bias light used. The humidity stability test was tested in a container with 15% relative humidity. The container was kept in the dark and the temperature was remained about 25  $^{\circ}\text{C}$ .

## References

1. Z. W. Zhu, G. S. Hu, B. G. Wang, A new method of measuring the characteristic viscosity for nylon-11, *Modern Plastics Processing and Applications* 2000, **12**, 32-33.