Supplementary Materials

Copper iodide as potential low-cost dopant for spiro-MeOTAD in perovskite solar cells

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Supporting Information 1

The cyclic voltammetry (CV) was performed with the three electrode system, using freshly distilled 1,2-dichlorobenzene with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) as electrolyte in a three-electrode system. The working electrode, the reference electrode, and the counter electrodes were a Pt wires, Ag/AgCl and Pt rods, respectively.

Supporting Information 2
The picture above: The color of spiro-MeOTAD is doped with different additions at 0 hour: 0# is added with Li-TFSI; 1#~3# with different concentrations of CuI and the concentration be increased gradually; 8# is added with FK209. The picture below: the same solution of the above store in the air after about 6 hour; for solution preparation of too little, so in 1#~3# we cannot see too much obvious precipitate.

**Supporting Information 3**

In this article, the spiro-OMeTAD+Cu solution is obtained by multiple filtering. We have added the above experiment detailed in the revised manuscript. The concentration of 20% CuI doped into the spiro-MeOTAD solution, and named as A1 solution. A1 solution is filtered to obtain B1 solution. And then, taking the B1 solution added to the dilute sulfuric acid and concentrated sulfuric acid are added into it and named as C1 solution and D1 solution, respectively. At last, the color of C1 solution has not change. The color of D1 solution becomes green. Then taking water added into D1, the color become similar to C1, cannot see any blue. If Cu was incompletely removed, when concentrated sulfuric acid is added into it, a chemical reaction has been happened as follows:

\[
Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 \uparrow + 2H_2O
\]

The CuSO₄ was soluble in water, and the color of solution is blue. So this result indicating that the Cu was completely removed.

Spiro-MeOTAD+Cu with precipitation was spin-coating on A 60 nm thick compact layer of TiO₂, then a 60 nm-thick Ag was deposited on the top of the HTM over layer by a thermal
evaporation. The presence of the copper metal in the hole-transporting layer of the device will be not covered with the silvers electrode. That is to say, the PCE of the perovskite films will be destroyed.

The precipitation is washed several times with ethanol in sequence. And then, the dilute sulfuric acid and concentrated sulfuric acid are added into it and named as D1 solution and E1 solution, respectively. At last, the color of D1 solution has not change. The color of E1 solution becomes blue and heat release. This result indicating that the precipitation is Cu.

When a small amount of the Cul is added into spiro-MeOTAD, this chemical reaction has been completely reaction and hasn’t any precipitation in the solution. With increasing of the concentration of the Cul, this reaction will be part of residue of the Cul. This experiment can be proved, as follows. In this article, the supernatant which has been filtered is employed as the precursor solutions of hole-transport material.

1) The concentration of 20% Cul doped into the spiro-MeOTAD solution and named as A1 solution. A1 solution is filtered to obtain B1 solution. And then, taking the B1 solution added to the aqueous solution of the sodium hydroxide (NaOH), followed by oscillating this solution named as C1 solution. We can observe that the color of the C1 solution becomes lighter and hasn’t any precipitation in the solution. For this reason is that the Iodide ion (I⁻) is easy to soluble in
inorganic solvent.

2) The concentration of 100% CuI doped into the spiro-MeOTAD solution and named as A2 solution. A2 solution is filtered to obtain B2 solution. And then, taking the B2 solution added to the aqueous solution of the sodium hydroxide (NaOH), followed by oscillating this solution named as C2 solution. Brick red colored precipitate is observed at once. This result indicates that a new substance is formed of C2 solution and named as Cu$_2$O. We can deduce that a chemical reaction has been happened as follows: Cu$^+$ + 2(OH)$^-$ → Cu$_2$O↓ + H$_2$O. We have added the above discussion in the revised manuscript.

![Images of B1 solution + NaOH, C1 solution, B2 solution + NaOH, C2 solution]

**Supporting Information 4**

Remarkably, compared with the acetonitrile is added to the surface of perovskite materials, the dipropyl sulfide may the minimum damage perovskite materials. This experiment can be further confirmed, as follows:

The chlorobenzene, tert-butylpyridine, acetonitrile and dipropyl sulfide are added to the surface of perovskite materials, respectively. When tert-butylpyridine and acetonitrile are added to the surface of perovskite materials, it can be clearly seen that the black of the perovskite films vanishes immediately, (the figure as follows). When chlorobenzene and dipropyl sulfide are added to the surface of perovskite materials, it can be clearly seen that the black of the perovskite films without any change (the figure as follows). After 30 minutes, these perovskite films are dried. We can also found that the black of the perovskite films without any change (the figure as follows). This results indicating that the chlorobenzene and dipropyl sulfide may the minimum damage
Impedance measurement of three different CuI doped concentration over frequency range of 0.1 Hz to 1M Hz under 0.983 Sun, AM1.5 illumination and perturbation 10mV.