Supporting Information

Reversible transformation of all-inorganic copper halide perovskite nanocrystals for anti-counterfeiting

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Experimental

Materials

Cesium iodide (CsI, 99.998%), copper halide (CuX, 99.999%) were obtained from Alfa. Cetyl-trimethylammonium tosylate (CTATos) was purchased from Sigma. Triethanolamine ($TEAH_3$) and tetraethyl-orthosilicate (TEOS) were obtained from TCI. Dimethylsulfoxide (DMSO, 99.5%) was provided by Sinopharm Chemical Reagent. SBA-15 was obtained from XFNANO. Al_2O_3 was purchased from Adamas. All chemicals were used as received without any further purification.

Preparation of SiO_2 nanospheres:

0.96 g CTATos and 0.16 g $TEAH_3$ were dissolved in 50 mL water at 80 ^oC, and then TEOS was quickly injected into the solution under vigorous stirring. After 2 hours, the acquired precipitate was washed using water and ethanol for 3 times, and then annealed at 550 ^oC for 6 hours to remove the organic components. After grinding, white SiO_2 powder was obtained.

Preparation of $Cs_3Cu_2I_5/SiO_2$:

CsI (0.3 M) and CuI (0.2 M) were dissolved in DMSO to obtain precursor solution. 50 mg SiO_2 powder was then mixed with 100 μL of the prepared solution, and then dried at 100 °C in vacuum to obtain $Cs_3Cu_2I_5/SiO_2$ powder.

Preparation of $Cs_3Cu_2I_5$ nanocrystals through hot-injection method:

$Cs_3Cu_2I_5$ nanocrystals were prepared following a reported procedure.[1] Typically, 0.1 mmol $Cu(OAc)_2$, 0.05 mmol Cs_2CO_3 and 1.6 mL oleic acid were mixed with 5 mL 1-octadecene in a glass vial. The vial was heated at 120 °C to completely dissolve the salts under vigorous stirring, followed by rapid injection of 0.8 mL oleylammonium iodide. After 10 s, the vial was cooled down to room temperature by using an ice water bath. $Cs_3Cu_2I_5$ nanocrystals were collected by centrifugation.

Phase transition:

A humidifier was employed to produce continuous and fine spray. The as-obtained blue-emitting $Cs_3Cu_2I_5/SiO_2$ was exposed to the spray treatment to realize the phase transition. When yellow-emissive $CsCu_2I_3/SiO_2$ was exposed to open air, it would recover to blue phase.

Scratch printing:

Typically, a sticker was attached on the substrate such as glass and paper, and then $Cs_3Cu_2I_5/SiO_2$ was filled in the hollow portion followed by scarping excess sample off. Next, the sticker template was removed and patterns was presented on the substrate.

Characterizations:

TEM and HRTEM images were collected on a 200 kV TECNAI G2 F20 with a Gatan SC200 CCD camera (FEI, USA). XRD were measured on a desktop diffractometer (D2 PHASER, Bruker, Germany) with a Cu Kα source. Absorption spectra were recorded by using a UV spectrometer (SPECORD S 600, Thermo Fisher, USA). PL measurement was carried out on a fluorescence spectrophotometer

(Fluoromax-4, Hamamatsu, Japan). Zeta potential was measured using a zeta potential analyzer (ELSZ-2000, Otsuka).

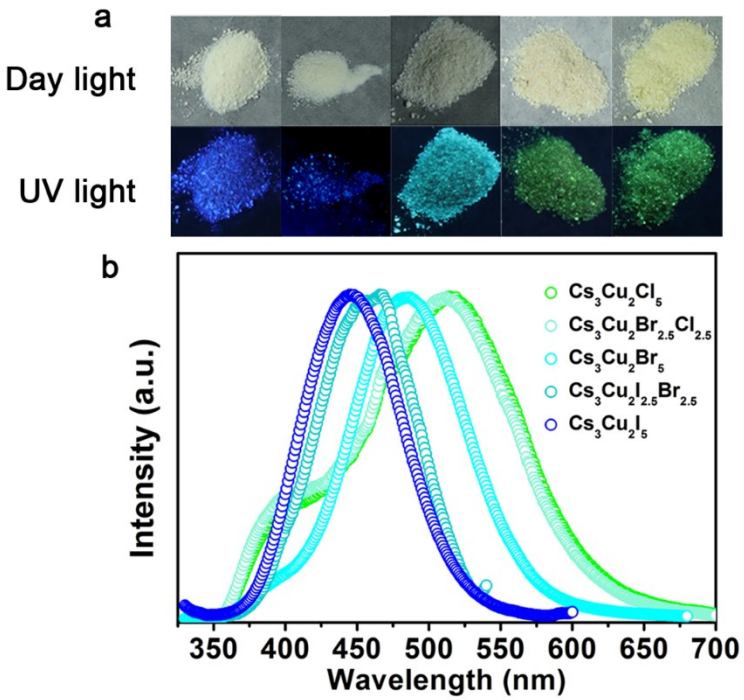

Fig. S1 (a) Photographs and (b) PL spectra of $Cs_3Cu_2X_5/SiO_2$ with different halide compositions.

Fig. S2 Mass production for $Cs_3Cu_2I_5/SiO_2$.

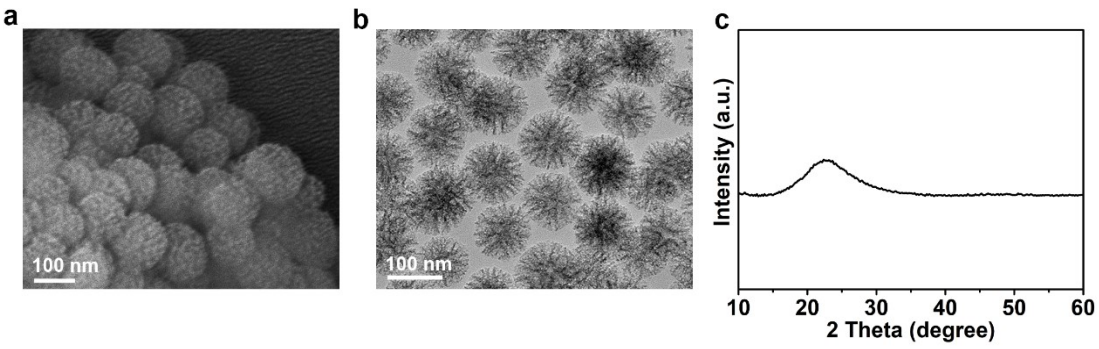

Fig. S3 (a) SEM, (b) TEM images and (c) XRD pattern of mesoporous SiO_2 nanospheres.

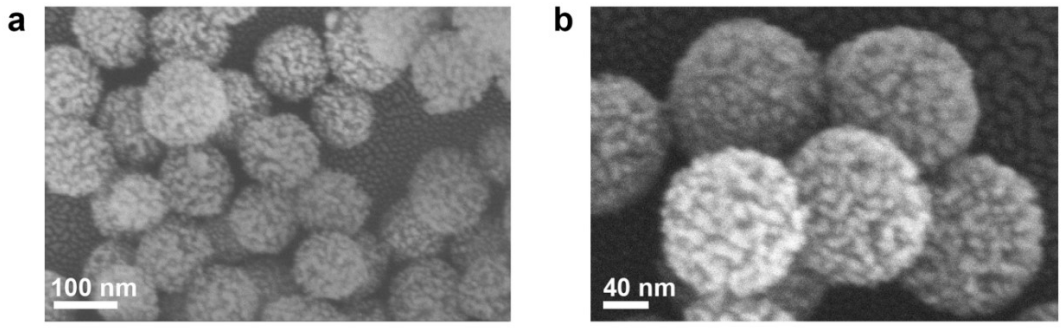

Fig. S4 SEM images of $Cs_3Cu_2I_5/SiO_2$ composite.

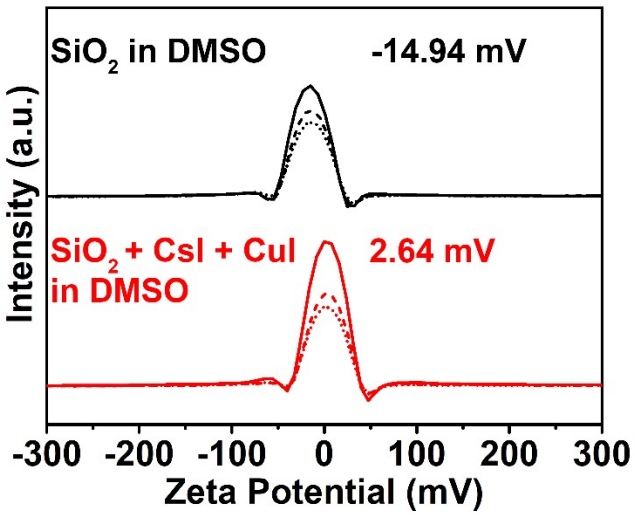

Fig. S5 Zeta potential of SiO_2 dispersed in DMSO and SiO_2 + CsI (0.03 M)+CuI (0.02 M) in DMSO. Each samples were tested for 3 times (presented as solid, dash, dotted line, respectively) under different applied voltage to determined the average zeta potential. Their average zeta potential was -14.94 mV and 2.64 mV, respectively.

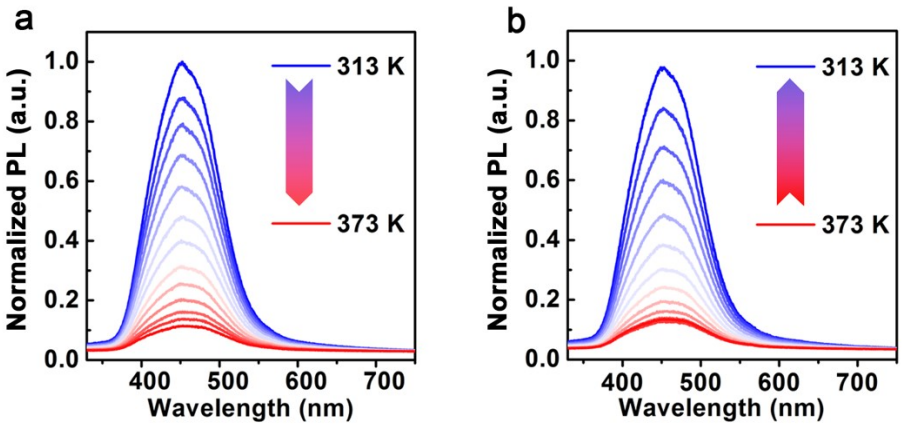

Fig. S6 Temperature-dependent PL emission spectra of $Cs_3Cu_2I_5/SiO_2$.

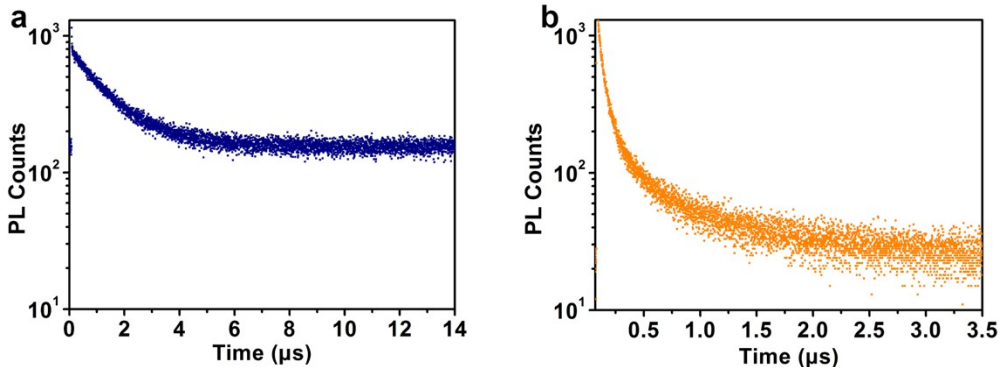

Fig. S7 PL decays of (a) $Cs_3Cu_2I_5/SiO_2$ and (b) $CsCu_2I_3/SiO_2$. The average PL lifetime of $Cs_3Cu_2I_5/SiO_2$ and (b) $CsCu_2I_3/SiO_2$ is 430 ns and 35 ns, respectively.

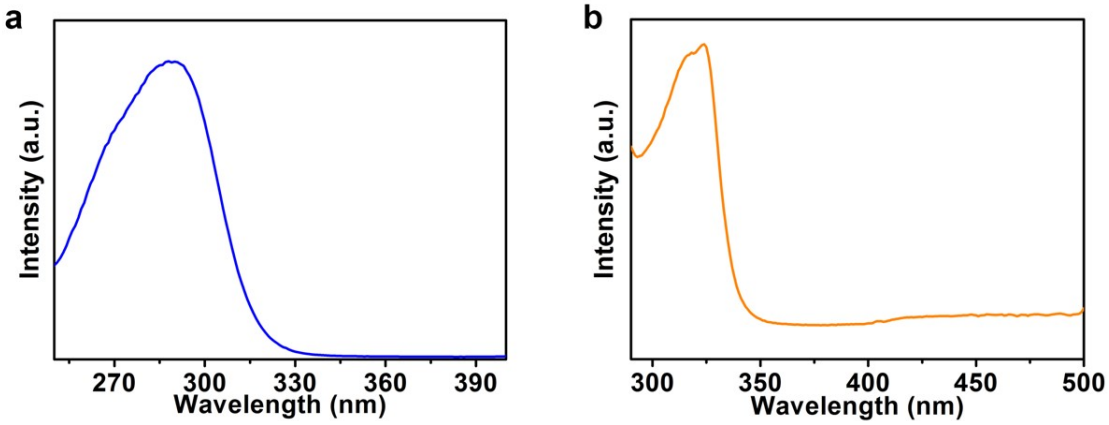

Fig. S8 PLE spectra of (a) $Cs_3Cu_2I_5/SiO_2$ and (b) $CsCu_2I_3/SiO_2$.

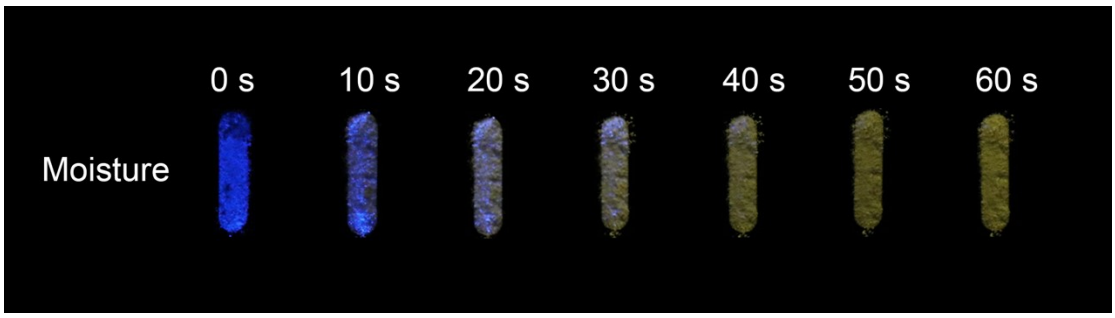

Fig. S9 Photographs of the transformation process from $Cs_3Cu_2I_5/SiO_2$ to $CsCu_2I_3/SiO_2$ under moisture treatment with a flow rate of 108 mg_{water} min^{-1}.

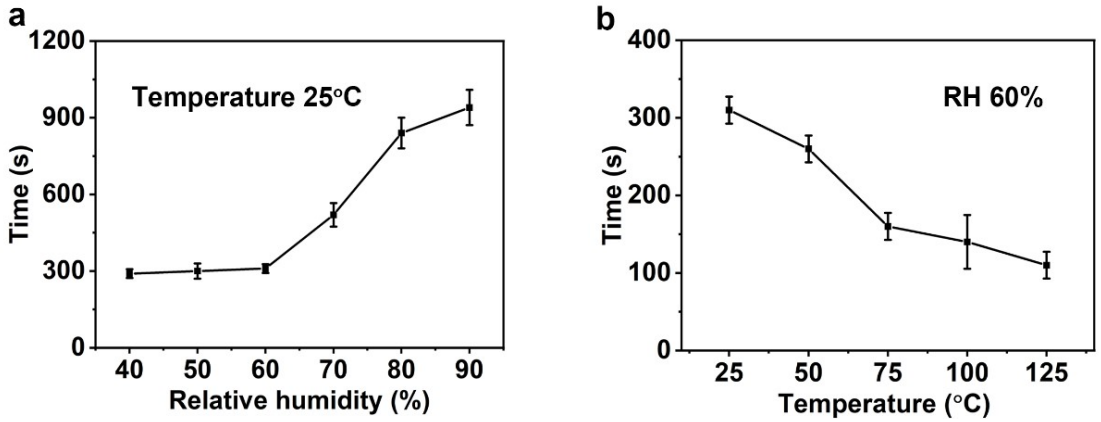

Fig. S10 Recovery time from $CsCu_2I_3/SiO_2$ to $Cs_3Cu_2I_5/SiO_2$ under different (a) relative humidity and (b) temperature. In (a), temperature was constant 25 °C. In (b), relative humidity was controlled as 60%.

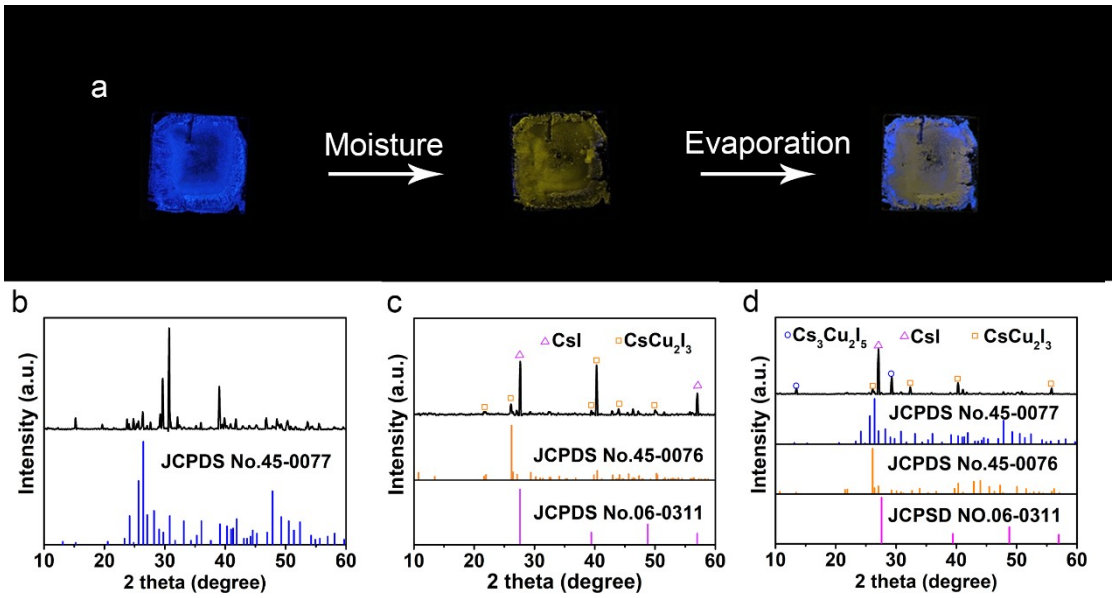

Fig. S11 (a) Photographs of bulk $Cs_3Cu_2I_5$ in one moisture treatment/evaporation cycle. XRD patterns of (b) intial, (c) moisture-treated and (c) recoverd samples by using bulk $Cs_3Cu_2I_5$ as the starting material.

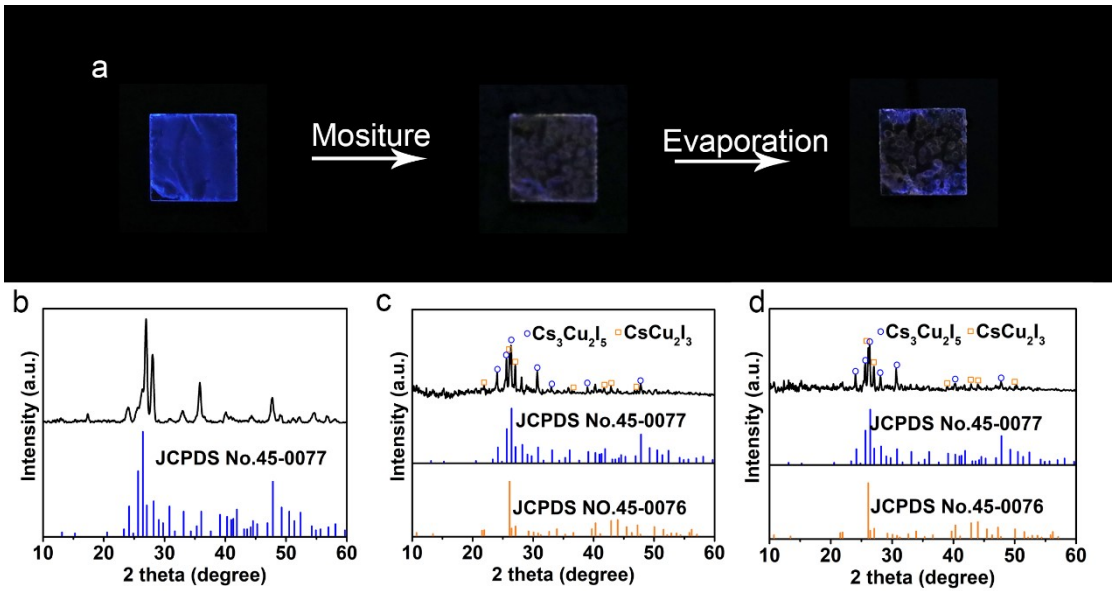

Fig. S12 (a) Photographs of $Cs_3Cu_2I_5$ nanocrystal film in one moisture treatment/evaporation cycle. XRD patterns of (b) intial, (c) moisture-treated and (c) recoverd samples by using $Cs_3Cu_2I_5$ nanocrystals as the starting material.

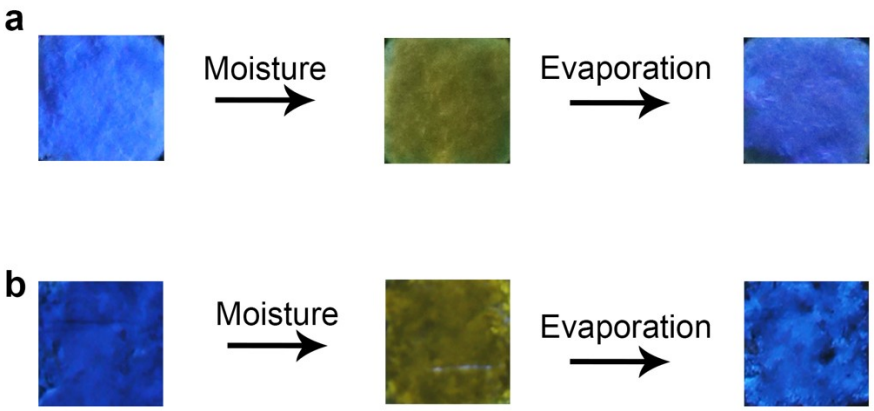

Fig. S13 Reversible phase transitions of (a) $Cs_3Cu_2I_5$/SBA-15 and (b) $Cs_3Cu_2I_5/Al_2O_3$ in one moisture treatment/evaporation cycle.

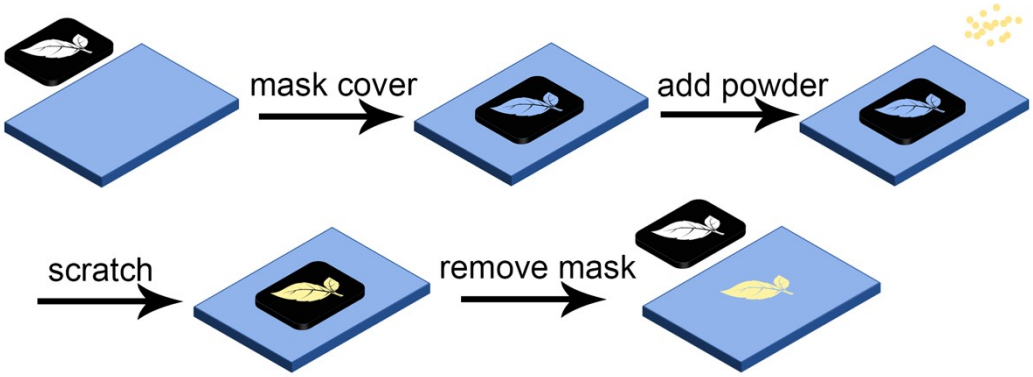

Fig. S14 Scheme illustration of scratch printing.

Table S1 Zeta potential values measured at different voltage.

	Voltage 1	Voltage 2	Voltage 3	Average
SiO_2 in DMSO	-15.96	-14.49	-14.37	-14.94
SiO_2+CsI+CuI in DMSO	2.98	2.60	2.32	2.64

Reference

1. Luo, Z. S.; Li, Q.; Zhang, L. M.; Wu, X. T.; Tan, L.; Zou, C.; Liu, Y. J.; Quan, Z. W., *Small*, 2020, **16**, 1905226.