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Controllable Synthesis of Cu-based quantum dots/nanocrystals and Application in White Light-Emitting Diodes

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Experimental Details

materials

Cuprous salt, Cs_2CO_3 and ethyl acetate (≥99.9%) are purchased from Aladdin. In(oAc)3 is purchased from Alfa Aesar and myristic acid (MA, AR≥99%) from Sigma. Dodecanethiol (DDT, 98%), 1-Octadence(ODE, ＞90%), oleic acid (OA, AR≥99%) Oleylamine (OAm, C18: 80–90%) and polymethyl methacrylate (PMMA) are purchased from Macklin. All the chemicals are used directly without any further purification.

$CuInS_2$/ZnS quantum dots

A typical four-step hot-injection procedure is as follows: firstly, a copper and sulfur precursor solution are prepared by dissolving 0.076 g CuI in 4 ml DDT and stir slightly at 60 °C. The color of the solution changes from milky to transparent and colorless. Secondly, 0.058 g $In(OAc)_3$, X (X = 0，0.1，0.2，0.3，0.4) mmol MA and 20 ml ODE are loaded into a 50 ml three-neck flask. Under Ar flow, the solution is degassed at 40 °C for 20 min and then heated to reaction temperature. Thirdly, 2.0 ml copper and sulfur precursor solution are swiftly injected into the reaction system to generate a large number of crystal seeds. The temperature is maintained for crystal seeds growth. The color of the solution changes from slightly green to yellow, blood red and finally brown dark in 1 h. The schematic diagram is shown in Fig. S1. (If the experiment is terminated at this time, $CuInS_2$ quantum dots are synthesized) At this time, 1.07 ml $Zn(OAc)_2$ solution can be slowly injected into the reaction solution. After a reaction time of 1 h, the product number is $CuInS_2$\ZnS. Finally, the $CuInS_2$\ZnS quantum dots is purified from the raw product by ethanol and ethyl acetate precipitation

followed by centrifugation and decantation for at least three times.

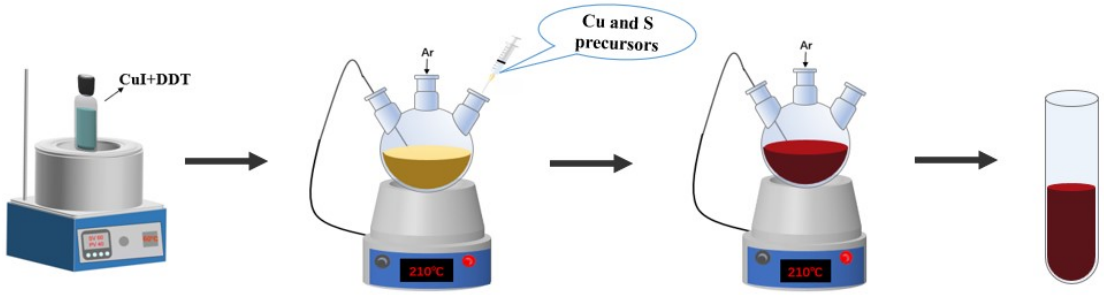

Fig. S1 Schematic of $CuInS_2$ quantum dots prepared via hot-injection method

Cs3Cu2X5 (X=Cl、 Br、I) nanocrystal

A mixture of CuX (1.5 mmol) and ODE (10 ml) was heated to 100 °C for 2 h under nitrogen environment to remove residual water in the drug, followed by adding 1 ml of OA and 1 ml of OAm to dissolve the CuX. Then, 1.1 mmol of Cs_2CO_3, 2 ml of OA, and 25 ml of ODE were mixed and heated to 100 °C, and kept under nitrogen environment for 2 h to remove residual water in the drug. Thereafter, the temperature was raised to 200 °C, and 5 ml of Cu^+ and X^- solution was injected to the Cs-OA precursor. After a reaction time of 10 s, an ice water bath was used to cool the reaction mixture. The original solution was taken out and centrifuged to obtain a precipitate, and finally the precipitate was dispersed in ethyl acetate and centrifuged again to leave a supernatant for subsequent characterization.

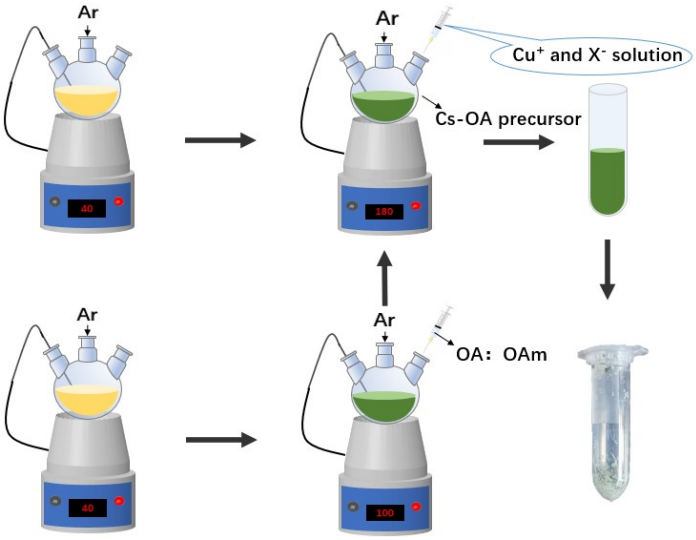

Fig. S2 Schematic of $Cs_3Cu_2X_5$（X=Cl、Br、I）nanocrystal prepared via reverse hot-injection method

Fabrication of LEDs

Firstly, the substrate glass was ultrasonically cleaned sequentially with ethanol and deionized water for 10 minutes, and then the substrate was irradiated with an ultraviolet-ozone cleaner for 10 min to remove the organic and impurity particles on the surface. Secondly, the previously prepared blue $Cs_3Cu_2I_5$ and green $Cs_3Cu_2Cl_5$ were mixed and dispersed in PMMA/chlorobenzene solution at a ratio of 1:1.5 to obtain GB paste. The prepared $CuInS_2$/ZnS QDs were mixed and dispersed in PMMA/ chlorobenzene solution at a certain molar mass ratio to obtain R paste. The process of preparing LEDs by remote coating encapsulation is shown in Fig. S3. The paste was transferred onto the glass substrate by scraping the first layer, then it was dried at 50°C and the organic solvent was volatilized. The second layer was printed on the first layer by following the same procedure. The LEDs were constructed by encapsulating $(GB)_nR_m$ coating on the UV-excited LED chip with an excited wavelength of 310 nm.

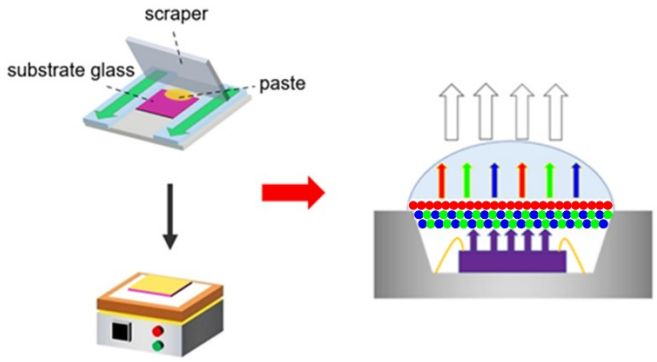

Fig. S3 The process of preparing LEDs via remote coating encapsulation techniques.

Characterized methods

The crystal structure of the sample was determined via X-ray diffraction (XRD) with a D8 Advance X-ray diffractometer (German), and the scanning rate was 2°/min. The Nicolet 6700 fourier transform infrared spectrometer (FTIR) was applied to observe the ligand infrared spectroscopy. The UV–vis absorption spectra was measured by using the UV-2600 UV–vis spectrophotometer (Japan). The photoluminescence excitation (PLE) spectrum and photoluminescence (PL) spectra are measured using the QM/TM/NIR spectrometer (China). The TEM, HRTEM and element plane scan figures were obtained by using the JEM-2100 transmission electron microscope (TEM, Japan) and the EDAX Elite energy-dispersive spectrometer (EDS), respectively. X-ray photoelectron spectra (XPS) are recorded by ESCALAB 250 Xi X-ray photoelectron spectrometer (America). The photoluminescence decay curves were estimated via a time-resolved fluorescence spectrometer detection system (America) together with

Spirit One 1040-8-SHG laser. The photoluminescence quantum yield (PLQY) was obtained by using an C9920-02G measurement system (Japan). The optical parameters of LEDs were measured by the integrating sphere (HAAS-2000, Everfine).

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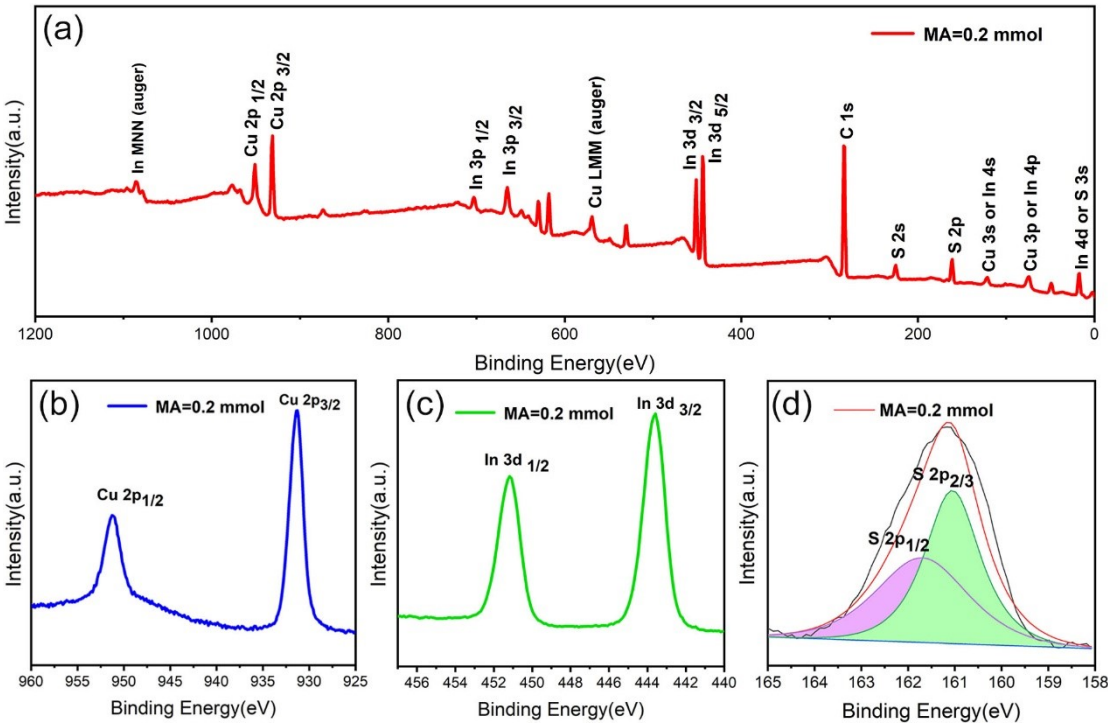

Fig. S4 XPS spectrum of as-prepared $CuInS_2$ quantum dots using 0.2 mmol MA: survey spectrum(a), Cu 2p (b), In 3d (c) and S 2p (d).

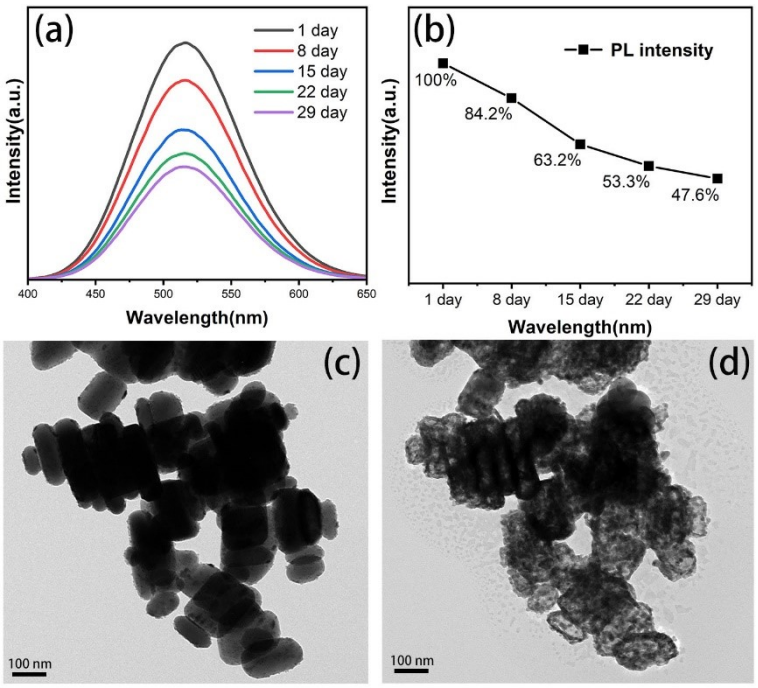

Fig. S5 PL spectra (a) and PL intensity (b) of $Cs_3Cu_2Cl_5$ nanocrystal with duration of placed in an ambient atmosphere; TEM images of $Cs_3Cu_2Br_5$ (c); TEM images of $Cs_3Cu_2Br_5$ with 30 s of placed under TEM irradiation (b).

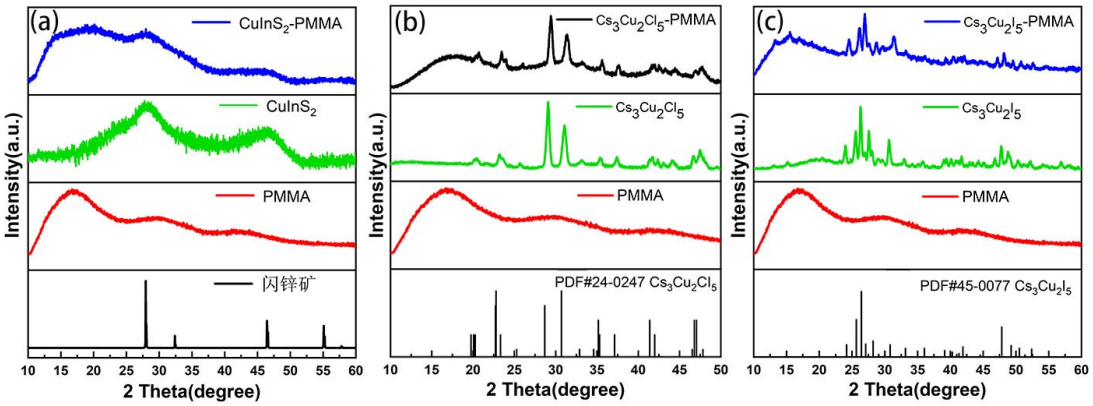

Fig. S6 XRD patterns of RGB trichromatic copper quantum dots/nanocrystals before and after miscibility with PMMA

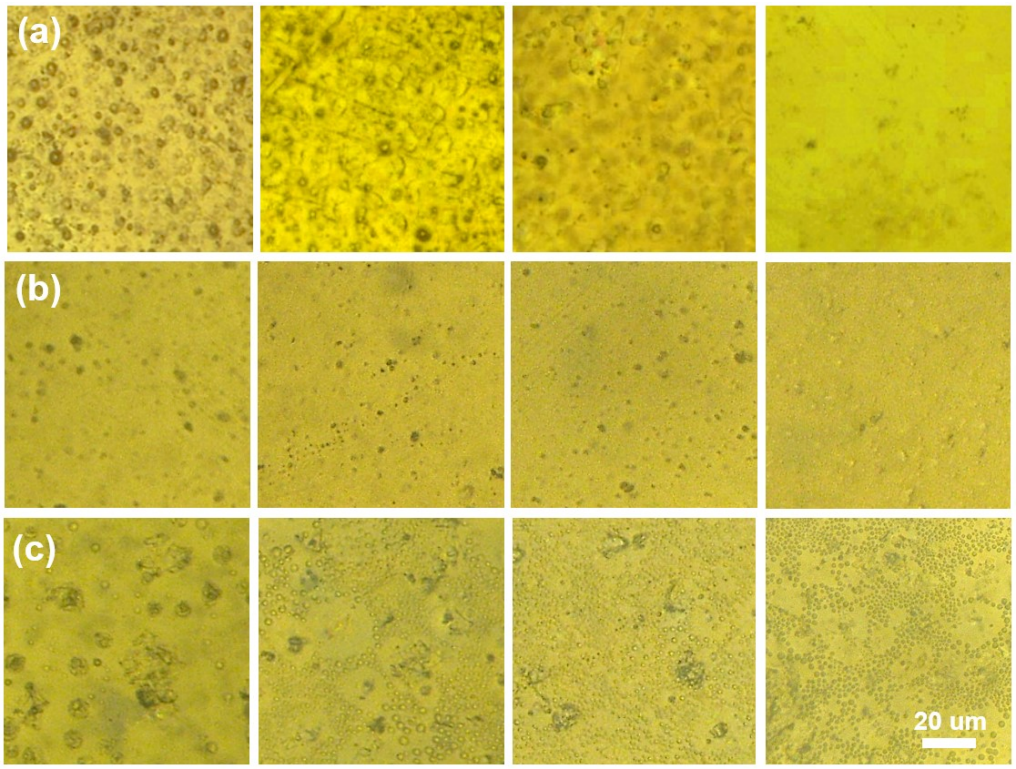

Fig. S7 Optical microscope photographs of $CuInS_2$/ZnS(a), $Cs_3Cu_2Cl_5$ (b), $Cs_3Cu_2I_5$ (c) after coating 1, 2, 3 and 4 layers respectively,

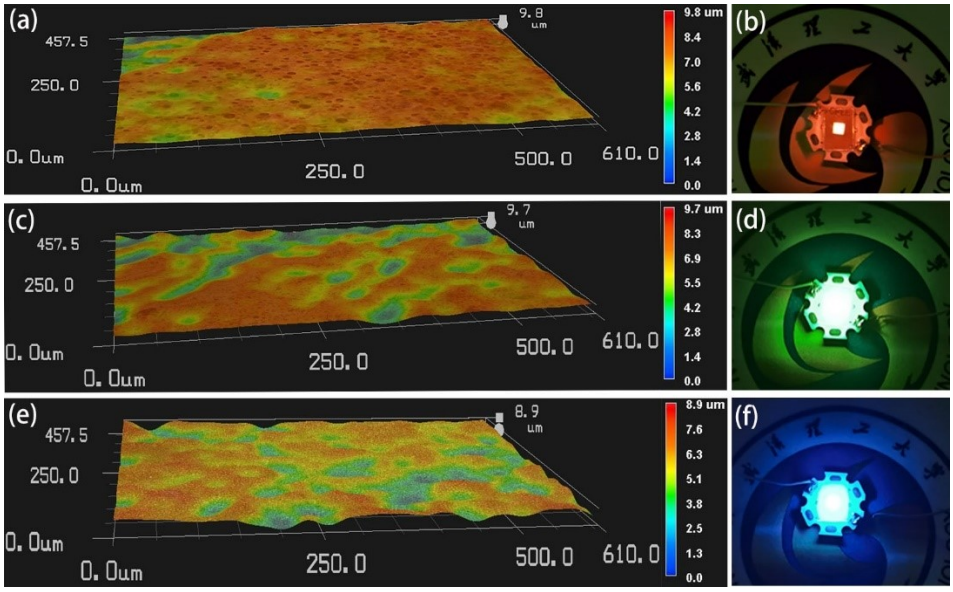

Fig. S8 3D optical microscope photographs and the corresponding LEDs lighting diagram of $CuInS_2$/ZnS (a, b) $Cs_3Cu_2Cl_5$ (c, d), $Cs_3Cu_2I_5$(e, f) after coating 4 layers.

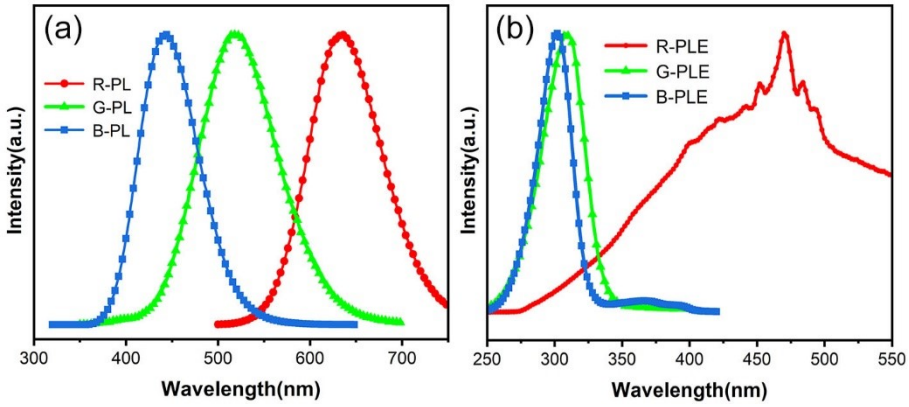

Fig. S9 PL (a) and PLE (b) spectra of RGB copper-based quantum dots/nanocrystals

Table S1 The space group and lattice constant of $Cs_3Cu_2Cl_5$, $Cs_3Cu_2Br_5$ and $Cs_3Cu_2I_5$

crystalline material	space groups	lattice parameters（Å）
$Cs_3Cu_2Cl_5$	Pnma	a = 9.478， b = 10.636，c = 13.303，α = β = γ = 90°
$Cs_3Cu_2Br_5$	Pnma	a =9.849， b = 11.106，c = 13.851，α = β = γ = 90°
$Cs_3Cu_2I_5$	Pnma	a = 10.420，b = 11.839，c = 14.593，α = β = γ = 90°

Table S2 Optical parameter of LEDs based on different layers

Number	CRI	CCT (K)	CIE
$(GB)_1R_1$	36.6	3499	(0.3924, 0.3605)
$(GB)_2R_1$	75.7	4615	(0.3575, 0.3665)
$(GB)_3R_1$	10.5	7515	(0.2850, 0.3734)
$(GB)_1R_2$	7.4	2256	(0.5575, 0.3674)
$(GB)_2R_2$	66.4	2189	(0.4499, 0.3530)
$(GB)_3R_2$	52.6	3578	(0.3746, 0.3176)