

Supporting Information

A Rapid Construction Strategy of NaYF₄:Yb,Er@CDs

Nanocomposites for Dual-Mode Anti-Counterfeiting

Haopeng Wei^{+1,2}, Yihao Zheng^{+*1,2}, Xingcai Zhang^{3,4}, Ping Liang^{1,2}, Xiaokai Xu^{1,2},
Chaofan Hu^{1,2}, Xuejie Zhang^{1,2}, Bingfu Lei^{1,2}, Yingliang Liu^{*1,2}, and Jianle
Zhuang^{*1,2}

¹ Key Laboratory for Biobased Materials and Energy of Ministry of Education/Guangdong Provincial Engineering Technology Research Center for Optical Agriculture, College of Materials and Energy, South China Agricultural University, Guangzhou 510642, China. E-mail: chemzhengyh@163.com; tliuy1@scau.edu.cn; zhuangjl@scau.edu.cn

² Guangdong Laboratory for Lingnan Modern Agriculture, Guangzhou 510642, China

³ School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, 02138, USA

⁴ School of Engineering, Massachusetts Institute of Technology, Cambridge, MA, 02139, USA

[+] These authors contributed equally to this work.

Experimental Section

Chemicals and Materials. Yttrium(III) chloride hexahydrate (99.99%), ytterbium(III) chloride hexahydrate (99.99%), erbium(III) chloride hexahydrate (99.995%), sodium chloride (99.5%), ammonium fluoride (98%), ethylene glycol (99%), N,N-dimethylformamide (DMF, 99.9%), dimethyl sulfoxide (DMSO, 99.8%) were purchased from Aladdin (Shanghai, China). Branched polyethylenimine (PEI, $M_w = 25000$) was purchased from Sigma-Aldrich (Shanghai, China). Citric acid (anhydrous, 99.5%) was purchased from Ourchem (Sinopharm Chemical Reagent Co., Ltd.). Thiourea (99.0%), sodium hydroxide (pellets, 96.0%), ethanol (anhydrous, 99.7%) were purchased from General-Reagent (Shanghai Titan Scientific Co., Ltd.). All reagents were used as received without further purification. Deionized water was used throughout this work.

Characterizations. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and energy dispersive spectrometry (EDS) elemental mapping were characterized on FEI Talos F200S and JEOL JEM-2100 F transmission electron microscope. X-ray diffraction (XRD) patterns were performed on a Rigaku Ultima IV X-ray diffractometer. Fourier transform infrared (FT-IR) spectra were collected with a Nicolet iS10 FT-IR spectrophotometer. Zeta potential was measured by a Zetasizer Nano ZSE. PL spectra and decay curves were recorded on an F-7000 spectrophotometer. UCL spectra and decay curves were measured with an Edinburgh FLS1000 spectrometer. UV-vis absorption spectrum was acquired on a Shimadzu UV-2550 spectrophotometer. All photographs under UV light and 980 nm laser were taken with a mobile phone.

Synthesis of CDs. The CDs were synthesized according to the reported methods with modifications.^{1,2} Specifically, 1 g of citric acid and 2.5 g of thiourea were dispersed in 10 mL of DMF with stirring for 10 min. The mixed solution was transferred to a 20 mL Teflon-lined stainless-steel autoclave and heated at 160 °C for 6 h. After cooling to

room temperature naturally, the resulting products were mixed with 20 mL of aqueous NaOH (50 mg/mL) and stirred for 5 min. After centrifugation at 18,000 rpm for 10 min, the supernatant was carefully removed with a pipette. The precipitate was washed twice with deionized water and centrifuged at 18,000 rpm for 10 min. Finally, the precipitate was collected and freeze-dried to obtain dark CDs powders.

Synthesis of NaYF₄:Yb,Er UCNPs. The NaYF₄:Yb,Er UCNPs were synthesized according to the reported methods with modifications.^{3,4} Firstly, YCl₃·6H₂O, YbCl₃·6H₂O, ErCl₃·6H₂O and NaCl were prepared into 0.78 M, 0.2 M, 0.02 M and 1 M aqueous solutions, respectively. The mixture solution of 0.78 mmol Y³⁺, 0.2 mmol Yb³⁺, 0.02 mmol Er³⁺, and 1 mmol NaCl was added into an aqueous solution containing 0.2 g PEI and 5 mL H₂O, and fully stirred for 5 min. Then, 20 mL ethylene glycol was slowly added and stirred for 30 min. Next, 1 mL of an aqueous solution containing 5 mmol NH₄F was added and stirred for 30 min. The resulting solution was transferred to a 100 mL PPL-lined (black) stainless-steel autoclave and heated at 160 °C for 12 h. After cooling to room temperature naturally, the precipitate was collected by centrifugation at 16,000 rpm for 10 min, then washed repeatedly (10 mL ethanol and 10 mL water) and centrifuged three times. Finally, the precipitate was dried in an oven at 60 °C for 10 h, and ground fully to obtain NaYF₄: Yb,Er UCNPs powders.

Synthesis of NaYF₄:Yb,Er@CDs nanocomposites. The preparation route of NaYF₄:Yb,Er@CDs is shown in Fig. S1. First, 1 mg CDs were dissolved in DMSO solvent at a concentration of 30 µg/mL. Next, 120 mg NaYF₄:Yb, Er powders were added to 10 mL DMSO solution of CDs in a centrifuge tube. After rapid manual shaking for half a minute, the mixture solution was allowed to stand for several minutes. After carefully removing the supernatant, the precipitate was collected and freeze-dried to obtain the NaYF₄:Yb,Er@CDs nanocomposites.

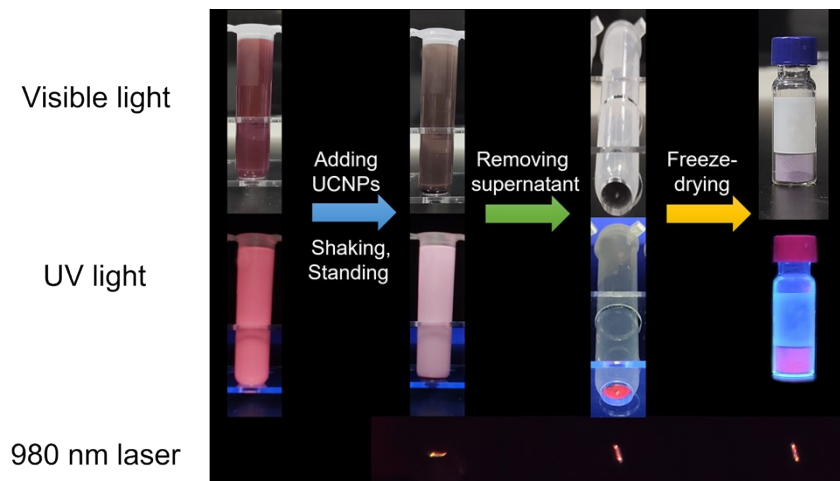


Fig. S1 The preparation procedure of NaYF₄:Yb,Er@CDs nanocomposites.

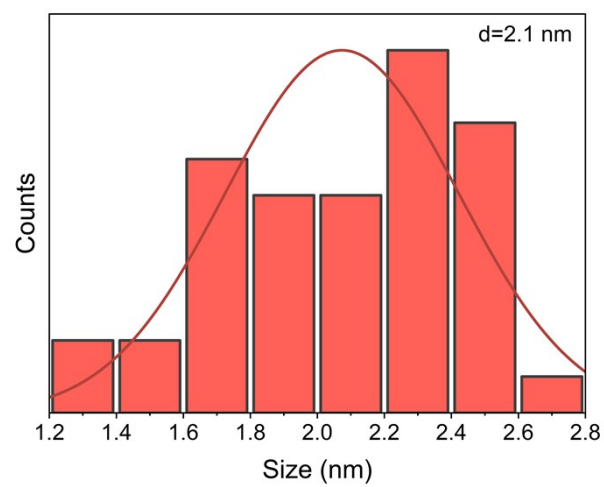


Fig. S2 The size distribution pattern of CDs.

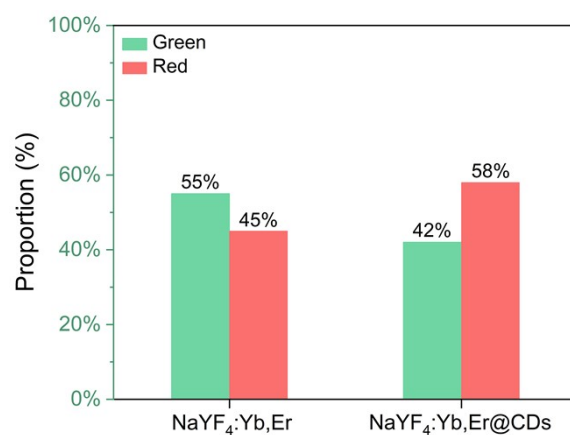


Fig. S3 Proportion of green and red emission of NaYF₄:Yb,Er and NaYF₄:Yb,Er@CDs.

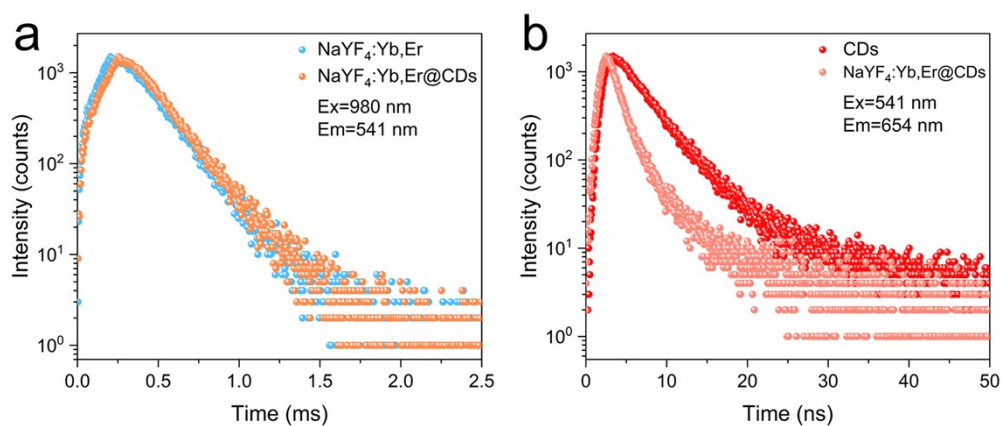


Fig. S4 The luminescence decay curves of NaYF₄:Yb,Er, CDs, and NaYF₄:Yb,Er@CDs.

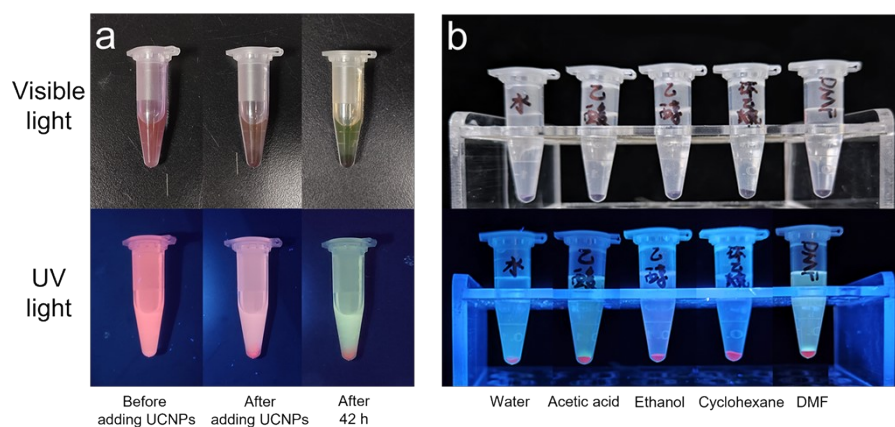


Fig. S5 (a) The photographs of the CDs solution before adding UCNPs, after adding UCNPs, and after 42 h. (Note: The green luminescence may be related to the deterioration caused by the long-time standing of the organic solvent DMSO.) (b) The photographs of NaYF₄:Yb,Er@CDs composites immersed in water, acetic acid, ethanol, cyclohexane, and DMF, respectively.

Table S1 Zeta potential values of NaYF₄:Yb,Er and CDs in deionized water.

Sample	Zeta potential (mV)
NaYF ₄ :Yb,Er	+40.3
CDs	-42.9
NaYF ₄ :Yb,Er@CDs	+10.8

Table S2 The lifetime data of NaYF₄:Yb,Er, CDs, and NaYF₄:Yb,Er@CDs at different excitation and emission wavelengths.

Sample	Lifetime (μ s)		Lifetime (ns)	
	Ex=980 nm	Em=541 nm	Sample	Ex=541 nm Em=654 nm
NaYF ₄ :Yb,Er	244		CDs	4.40
NaYF ₄ :Yb,Er@CDs	233		NaYF ₄ :Yb,Er@CDs	1.70

References

- 1 D. Qu, Z. Sun, M. Zheng, J. Li, Y. Zhang, G. Zhang, H. Zhao, X. Liu and Z. Xie, *Adv. Opt. Mater.*, 2015, **3**, 360–367.
- 2 H. Li, D. Su, H. Gao, X. Yan, D. Kong, R. Jin, X. Liu, C. Wang and G. Lu, *Anal. Chem.*, 2020, **92**, 3198–3205.
- 3 G. Tian, L. Duan, X. Zhang, W. Yin, L. Yan, L. Zhou, X. Liu, X. Zheng, J. Li, Z. Gu and Y. Zhao, *Chem. Asian J.*, 2014, **9**, 1655 – 1662.
- 4 D. Zhang, L. Wen, R. Huang, H. Wang, X. Hu and D. Xing, *Biomaterials*, 2018, **153**, 14-26.