

PAA modified upconversion nanoparticles for highly selective and sensitive detection of Cu²⁺ ions

Shaoshan Su, Zhurong Mo, Guizhen Tan, Hongli Wen*, Xiang Chen*, D. A. Hakeem*

Key Laboratory of Clean Chemistry Technology of Guangdong Regular Higher Education Institutions, School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, P.R. China

*Corresponding author:

E-mail addresses: hongliwen@gdut.edu.cn (H. Wen); chenxiang@gdut.edu.cn (X. Chen); abdulhakeem.desh@gdut.edu.cn (D. A. Hakeem)

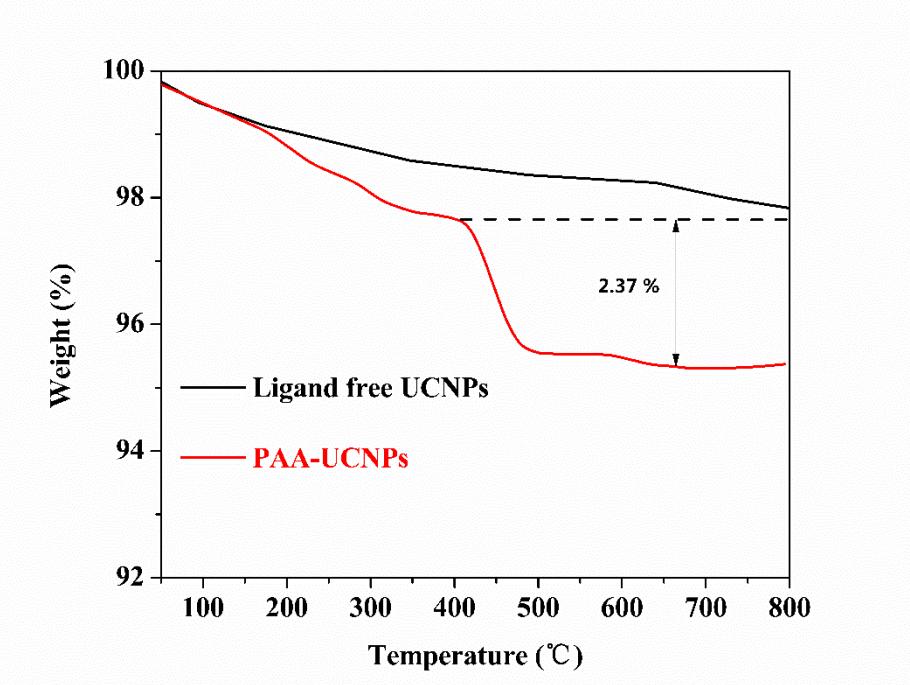


Fig. S1 TGA curves of ligand free $\text{NaYb}_{0.5}\text{Nd}_{0.5}\text{F}_4 @ \text{NaYb}_{0.5}\text{Gd}_{0.49}\text{Tm}_{0.01}\text{F}_4 @ \text{NaGdF}_4$ UCNPs and PAA coated $\text{NaYb}_{0.5}\text{Nd}_{0.5}\text{F}_4 @ \text{NaYb}_{0.5}\text{Gd}_{0.49}\text{Tm}_{0.01}\text{F}_4 @ \text{NaGdF}_4$ UCNPs, respectively.

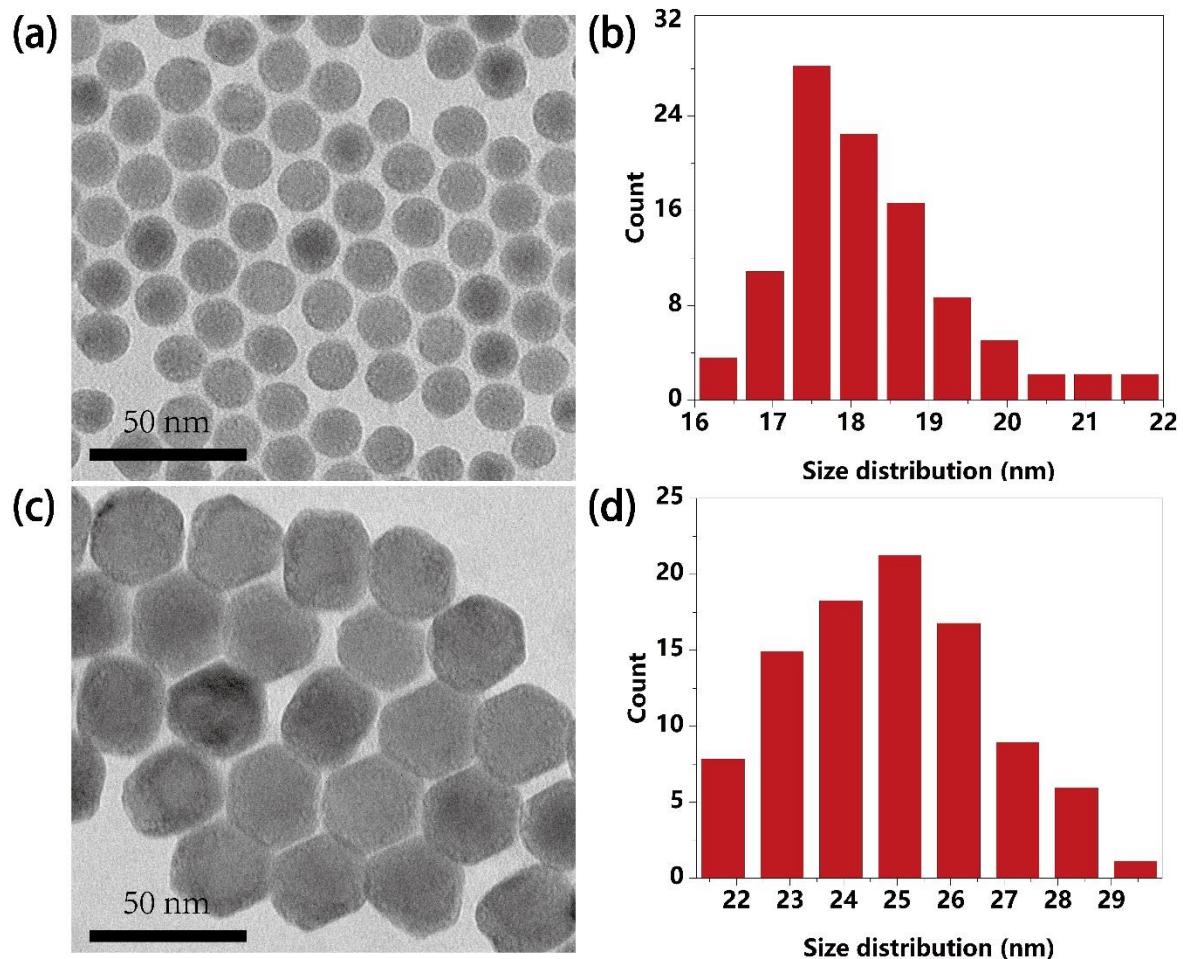


Fig. S2 TEM images (a and c) and size distribution (b and d) of the as-prepared core of $\text{NaYb}_{0.5}\text{Nd}_{0.5}\text{F}_4$ and core-shell structure with composition of $\text{NaYb}_{0.5}\text{Nd}_{0.5}\text{F}_4@\text{NaYb}_{0.5}\text{Gd}_{0.49}\text{Tm}_{0.01}\text{F}_4$ nanoparticles, respectively.

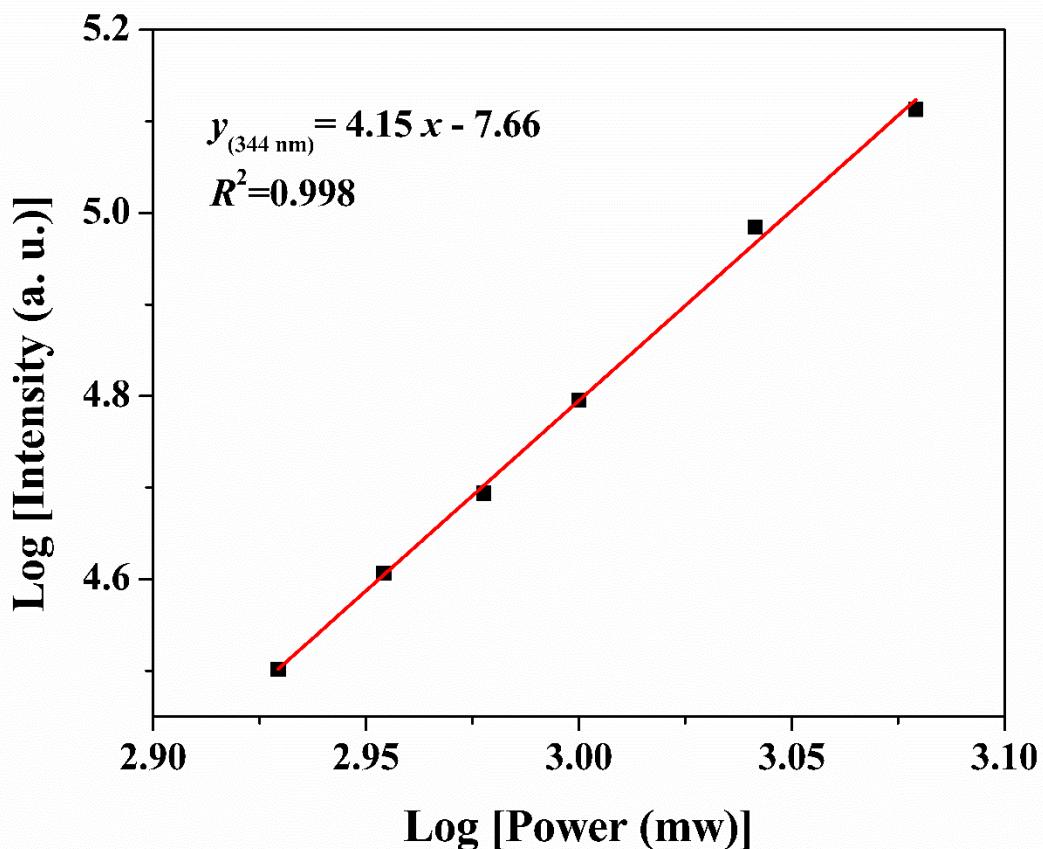


Fig. S3 Double-logarithmic plots of the pump-power dependent upconversion emission intensity from Tm^{3+} emission at 344 nm recorded under 980 nm excitation.

Table S1. Comparison of the PAA-UCNPs nanoplatform with the other reported platforms for the Cu²⁺ detection.

Probes	Analytes/excitation wavelength	LOD	Linear range	reference
PAA- NaYb _{0.5} Nd _{0.5} F ₄ @NaYb _{0.5} Gd _{0.49} T m _{0.01} F ₄ @NaGdF ₄	Cu ²⁺ / 980 nm	0.1 μM	0.125–3.125 μM	This work
TPEA-Carbon quantum dots	Cu ²⁺ / 405 nm	10 nM	10 ⁻⁶ –10 ⁻⁴ M	1
Rhodamine B-SiO ₂ coated NaYF ₄ :Yb,Er@NaYF ₄	Cu ²⁺ / 520 nm	0.82 μM	-	2
Carboxyl-modified CdTe QDs	Cu ²⁺ / 340 nm	0.36 nM	0 to 100 nM	3
PEI-capped NaGdF ₄ :Yb/Tm	Cu ²⁺ / 980 nm	57.8 nM	0.1-2 μM	4
TSPP-NaYF ₄ :Yb,Er,Gd@SiO ₂	Cu ²⁺ / 980 nm	2.16 μM	5 μM–0.16 mM	5
Rd-NH ₂ -β-NaYF ₄ :Yb ³⁺ /Er ³⁺	Cu ²⁺ / 980 nm	-	2–14 μM	6
RB-hydrazide-NaYF ₄ :Yb ³⁺ /Er ³⁺	Cu ²⁺ / 980 nm	10 ⁻⁶ M	10 ⁻⁵ to 10 ⁻⁶ M	7

*TPEA = ([N-(2- aminoethyl)-N,N,N' -tris(pyridin-2-ylmethyl)

TSPP = meso-tetra(4-sulfonatophenyl)porphine dihydrochloride

Rd-NH₂ = 2-amino-3',6'-bis(ethylamino)-2',7'-dimethyl-3',9a'-dihydrospiro[isoindoline-1,9'-xanthen]-3-one

References:

1. Q. Qu, A. Zhu, X. Shao, G. Shi and Y. Tian, Development of a carbon quantum dots-based fluorescent Cu²⁺ probe suitable for living cell imaging, *Chem. Commun.*, 48(2012)5473-5475.
2. Y.X. Xu, H.F. Li, X.F. Meng, J.L. Liu, L.N. Sun, X.L. Fan, L.Y. Shi, Rhodamine-modified upconversion nanoprobe for distinguishing Cu²⁺ from Hg²⁺ and live cell imaging, *New J. Chem.*, 40(2016)3543-3551.
3. Y.H. Wang, C. Zhang, X.C. Chen, B. Yang, L. Yang, C.L. Jiang, Z.P. Zhang, Ratiometric fluorescent paper sensor utilizing hybrid carbon dots–quantum dots for the visual determination of copper ions, *Nanoscale*, 8(2016)5977-5984.
4. F. Wang, C. Zhang, Q. Xue, H. Li, Y. Xian, Label-free upconversion nanoparticles-based fluorescent probes for sequential sensing of Cu²⁺, pyrophosphate and alkaline phosphatase activity, *Biosens. Bioelectron.*, 95(2017)21-26.
5. X. Huang, L. Wang, X. Zhang, X. Yin, N. Bin, F. Zhong, et al., Dye-assembled nanocomposites for rapid upconversion luminescence sensing of Cu²⁺, *Sens. Actuators B Chem.*, 248(2017)1-8.
6. X. Jiang, G. Meng, A rhodamine-based sensing probe excited by upconversion NaYF₄:Yb³⁺/Er³⁺ nanoparticles: The realization of simple Cu(II) detection with high sensitivity and unique selectivity, *J. Lumin.*, 135(2013)227-231.
7. J. Zhang, B. Li, L. Zhang, H. Jiang, An optical sensor for Cu(ii) detection with upconverting luminescent nanoparticles as an excitation source, *Chem. Commun.*, 48(2012)4860-4862.