Rational Synthesis of Three-dimensional Core-double Shell Upconversion Nanodendrites with Ultrabright Luminescence for Bioimaging Application

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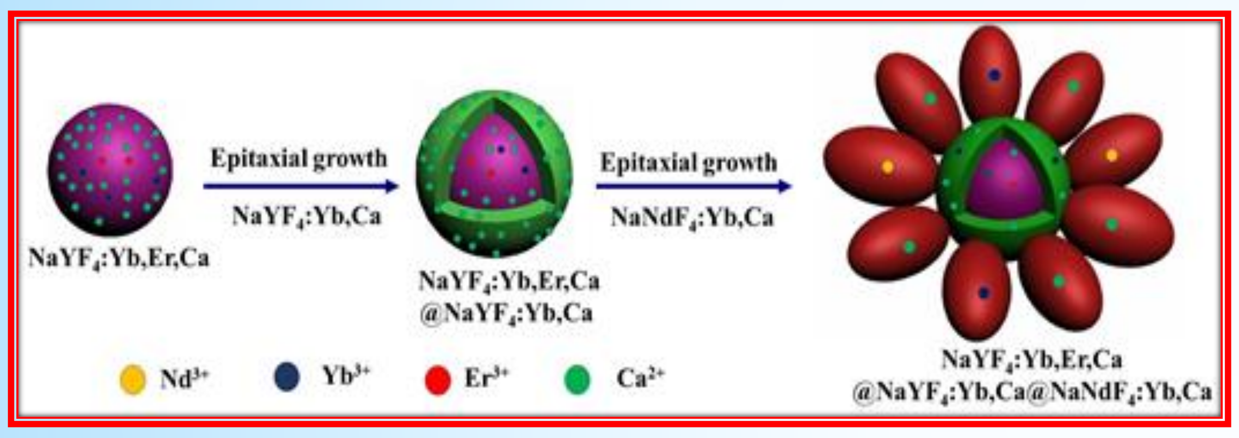
Abstract

Engineering the morphology of rare-earth doped $NaYF_4$-based upconversion nanoparticles (UCNPs) can effectively tune their upconversion luminescence emissions (UCLE) properties. Herein, we rationally synthesized a new class of three-dimensional upconversion core-double-shell nanodendrites (UCNDs) including an active core ($NaYF_4$: Yb, Er, Ca) capped by a transition layer ($NaYF_4$: Yb, Ca) and an active outer shell ($NaNdF_4$: Yb, Ca). The high concentration of Nd^{3+} sensitizer in the outer dendritic shell enhances the luminescence intensity, while the transition layer enriched with Yb^{3+} acts as an efficient energy migration network between the outer shell and inner core along with preventing the undesired quenching effects resulting from Nd^{3+}. These unique structural and compositional merits enhanced the UCLE of UCNDs by 5 and 15 times relative to $NaYF_4$: Yb, Er, Ca@$NaYF_4$: Yb, Ca truncated core-shell UCNPs and $NaYF_4$: Yb, Er, Ca spherical core UCNPs, respectively under excitation at 980 nm. The SiO_2-COOH layer coated UCNDs (UCND@SiO_2-COOH) were successfully used as efficient long-term luminescence probes for the *in vitro* and *in vivo* bioimaging without any significant toxicity. The uptake and retention of UCND@SiO_2-COOH were almost found in the liver and spleen. This study may open the way towards preparation of spatial UCNDs nanostructures for biomedical applications.

Results and discussion



Scheme 1. The fabrication process of UCNDs**.**

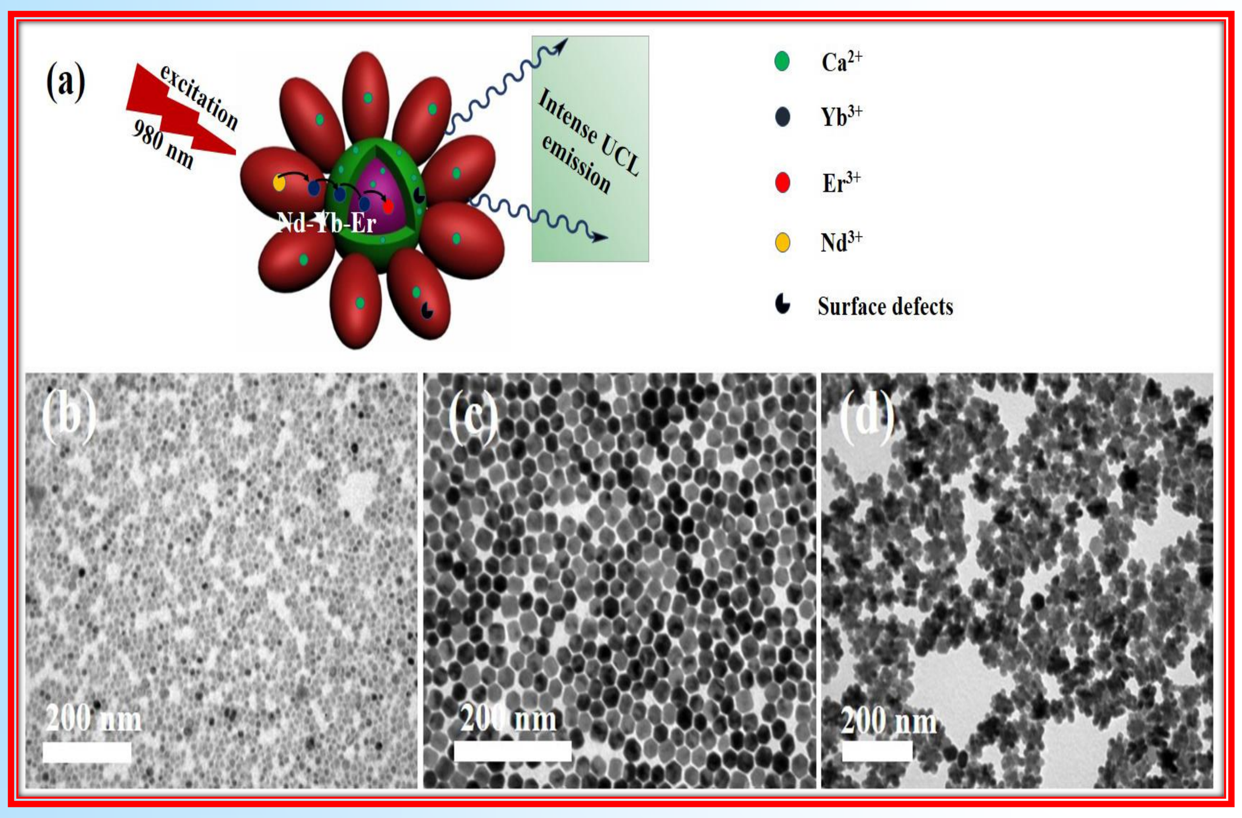


Fig. 1. (a). Schematic diagram of UCNDs composed of a core-double shell with their ability to absorb and transfer energy along with suppressing luminescence quenching. TEM images of (b) UCNPs core, (c) UCNPs core-shell and (d) UCNDs core-double shell.

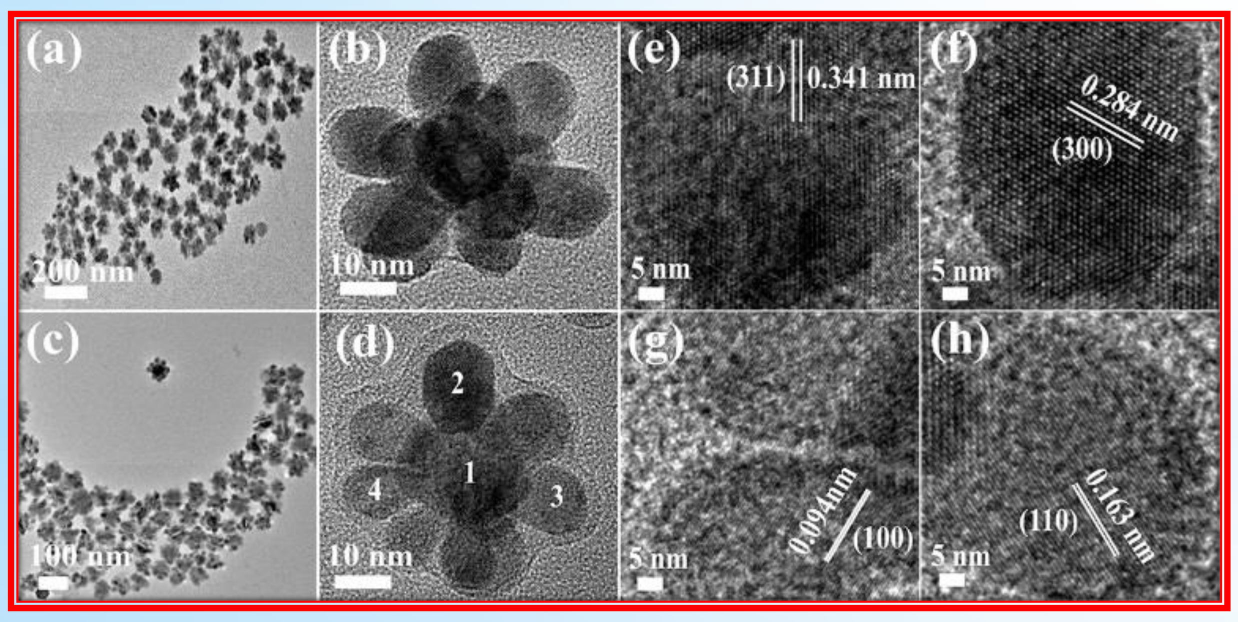


Fig. 2. (a) TEM image and (b) HRTEM image of UCNDs. (C) TEM image and (d) HRTEM image of UCND@SiO_2-COOH. (e-h) HRTEM images recorded form the numbered areas in (d).

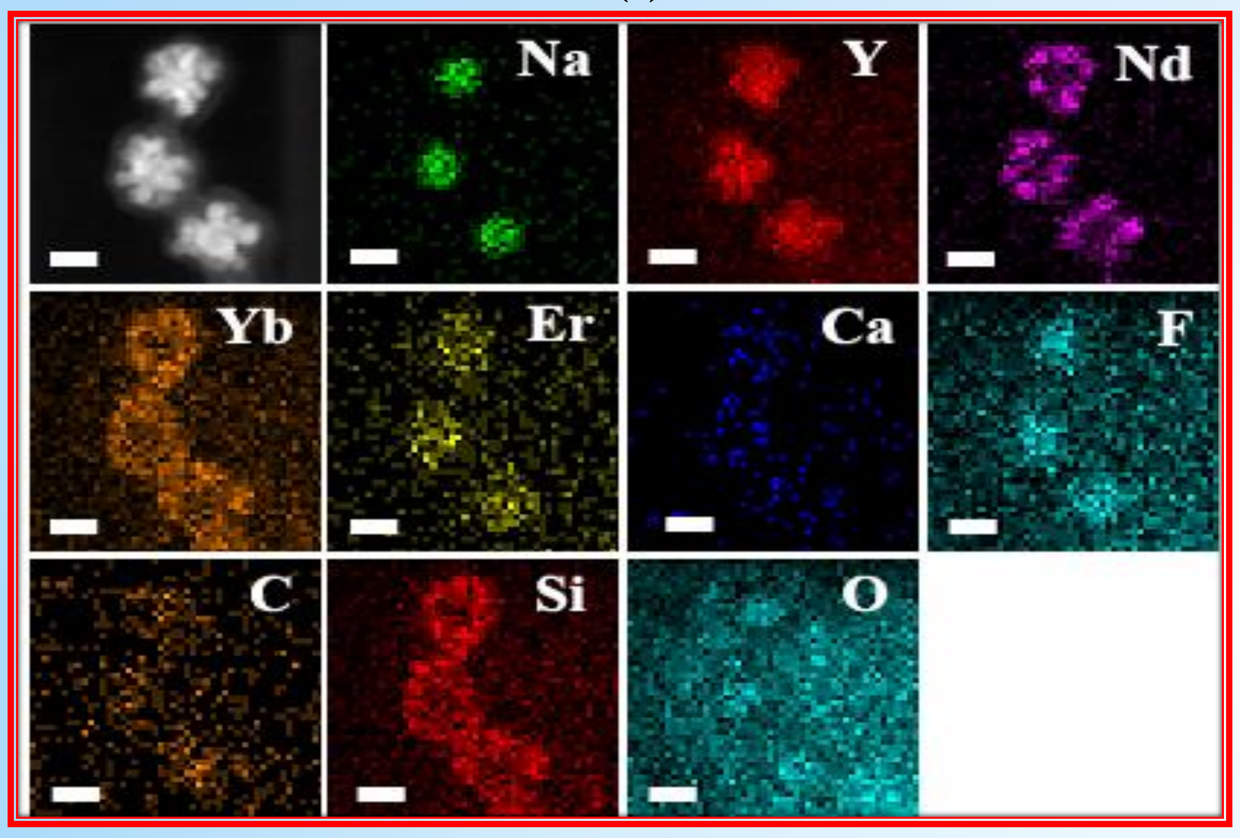


Fig. 3. HAADF-STEM images of and element mapping analysis of the UCND@SiO_2-COOH and (b) UCNDs. The indicated scale bars are 50 nm.

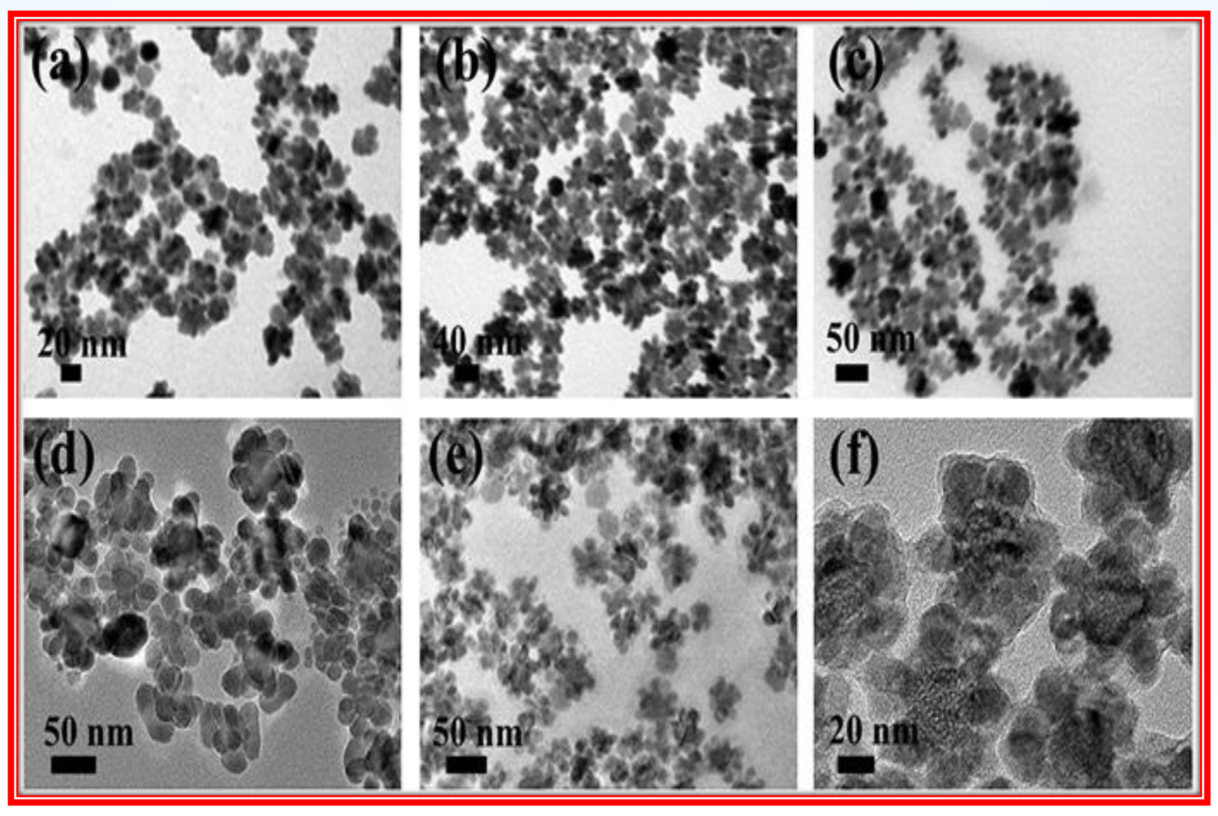
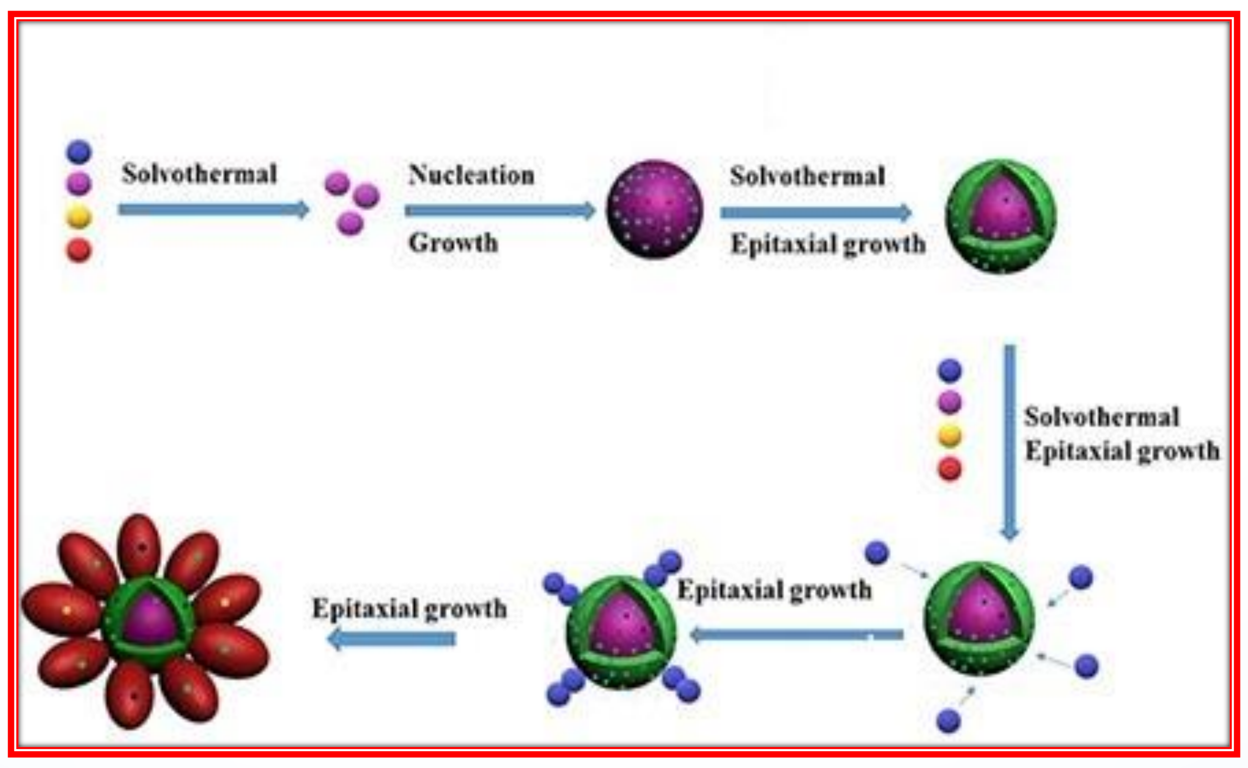


Fig. 4. TEM images of UCNDs collected at different reaction times (a-c). UCNDs prepared using different concentrations of $NdCl_3$ (d) (0.5 mol L^{-1}, 0.5 mL), (e) (1 mol L^{-1}, 0.5 mL), and (f) (2 mol L^{-1}, 0.5 mL).



Scheme. 2. The proposed production mechanism of UCNDs.

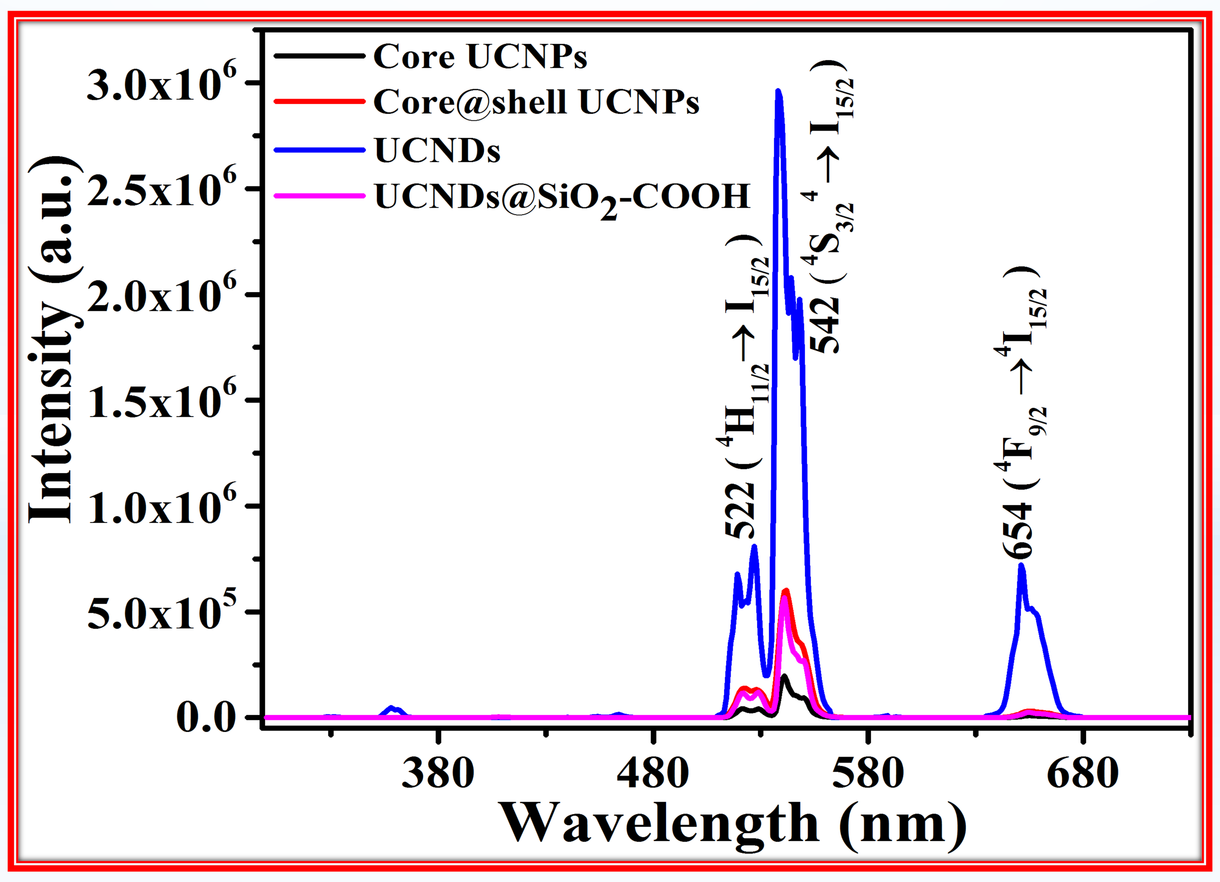


Fig. 5. The UCLE spectra under 980 nm excitation.

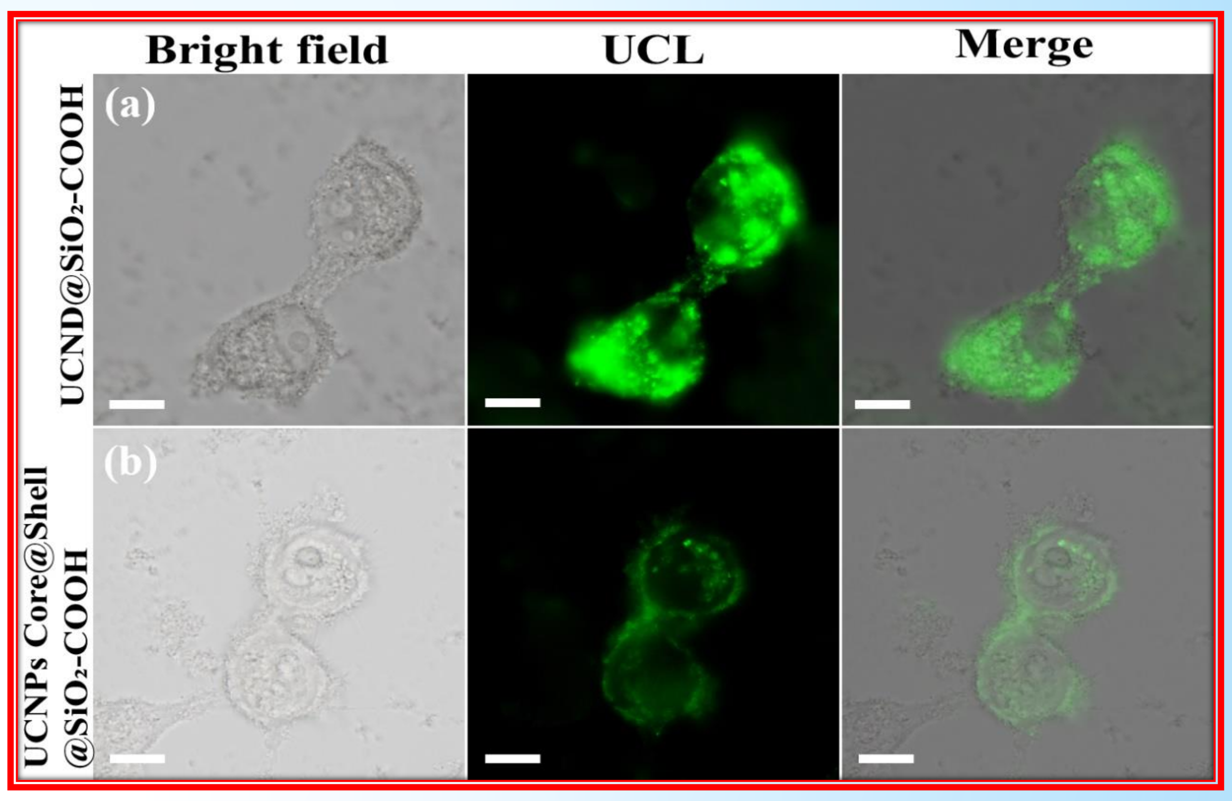


Fig. 6. High-resolution confocal fluorescence microscopy images of HeLa cells treated with 100 µg mL^{-1} of (a) UCND@SiO_2-COOH and (b) UCNPs core@shell@SiO_2-COOH for 24 h. The indicated scale bars are 10 µm.

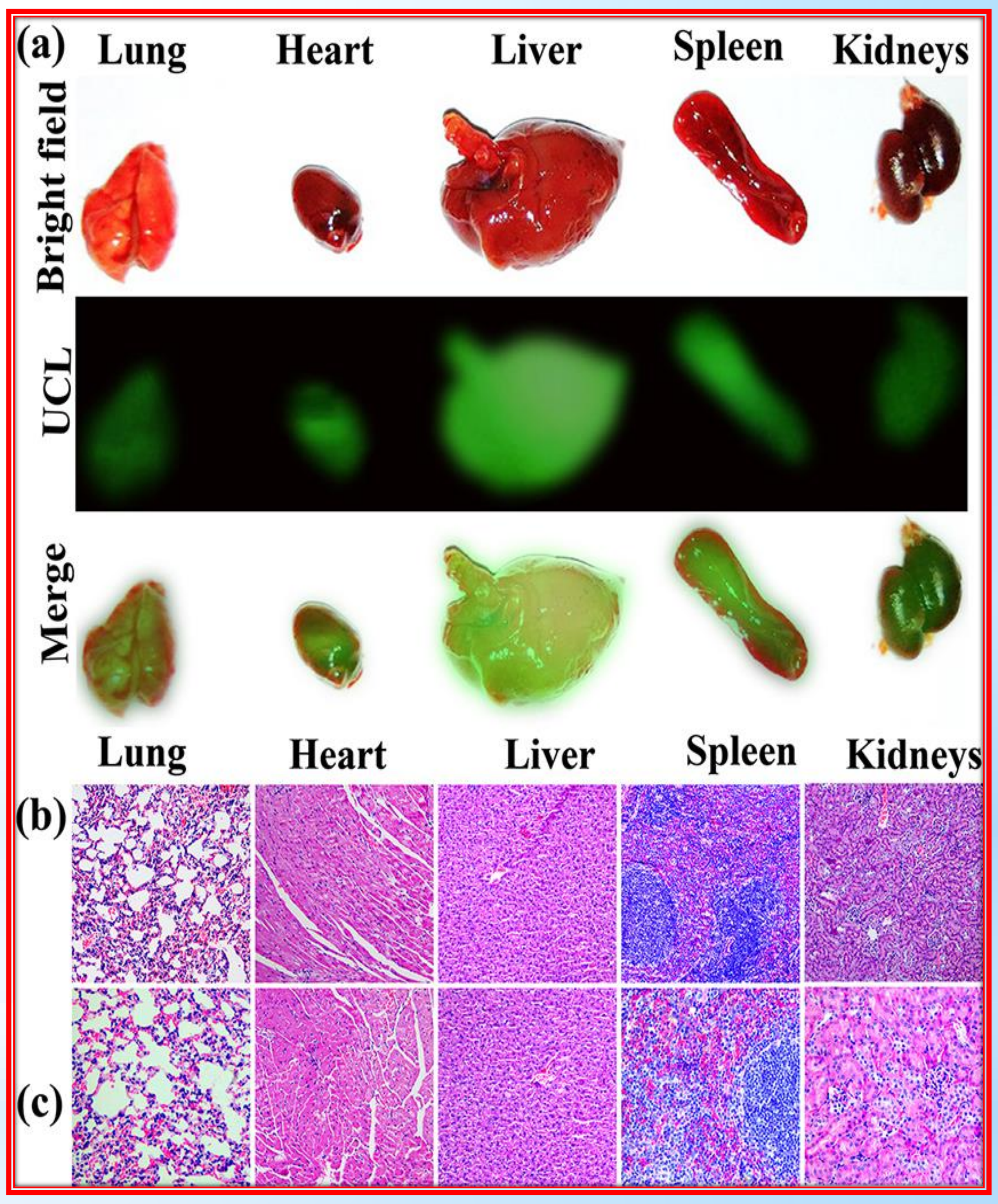


Fig. 7. (a) Ex vivo UCL imaging of different organs collected from the BALB/c mouse injected with (10 mg kg^{-1} bodyweight) of UCND@SiO_2-COOH. Histological analysis of tissues collected from the organs of (b) untreated mouse and (c) treated mouse.

Conclusion

we rationally designed spatial UCNDs core-double shell with multiple branched arms. The Nd^{3+} with a high content enriched the outer shell enhances the absorption energy, while the middle layer acts as a protective shield for preventing the quenching interaction between Er^{3+} and Nd^{3+}. Meanwhile, Yb^{3+} in the middle layer maintains the efficient excitation energy transfer between Nd^{3+} and Er^{3+}. These unique structural and compositional merits enhanced the UCLE of UCNDs by 5 and 15 times compared to core-shell UCNPs and core UCNPs, respectively at 980 nm. The carboxy-terminated silica shell coated UCNDs (UCND@SiO_2-COOH) were utilized successfully as luminescence probes for *in vitro* and *in vivo* bioimaging without any significant toxicity.

References

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