Tuning Luminescence of $NaYF_4$:Ln (Ln = Nd, Er, Tm, and Yb) based upconversion nanoparticles

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Introduction

In recent years, multifunctional nanoparticle has been widely demanded in the bio-medical field due to its prominent feature of serving multiple functions simultaneously. Particularly, manipulation of various neuronal modulations by activating optically and mechanically sensitive ion channels has been widely researched.

For optical bioprobes, lanthanide doped upconversion nanoparticle (UCNP) has gained attention as it is able to sequentially absorb two or more photons of low-energy near infrared radiation (NIR) light and emit one photon of higher energy light in the visible range. Anti-Stokes fluorescence for NIR excitation is very significant in biological sample as it not only has good signal to noise ratio, but also deep penetration depth and low toxicity in biological tissues. Especially, multiple labeling allows for efficient bioimaging which is achieved by fluorescent particle with different emissions under the same excitation.

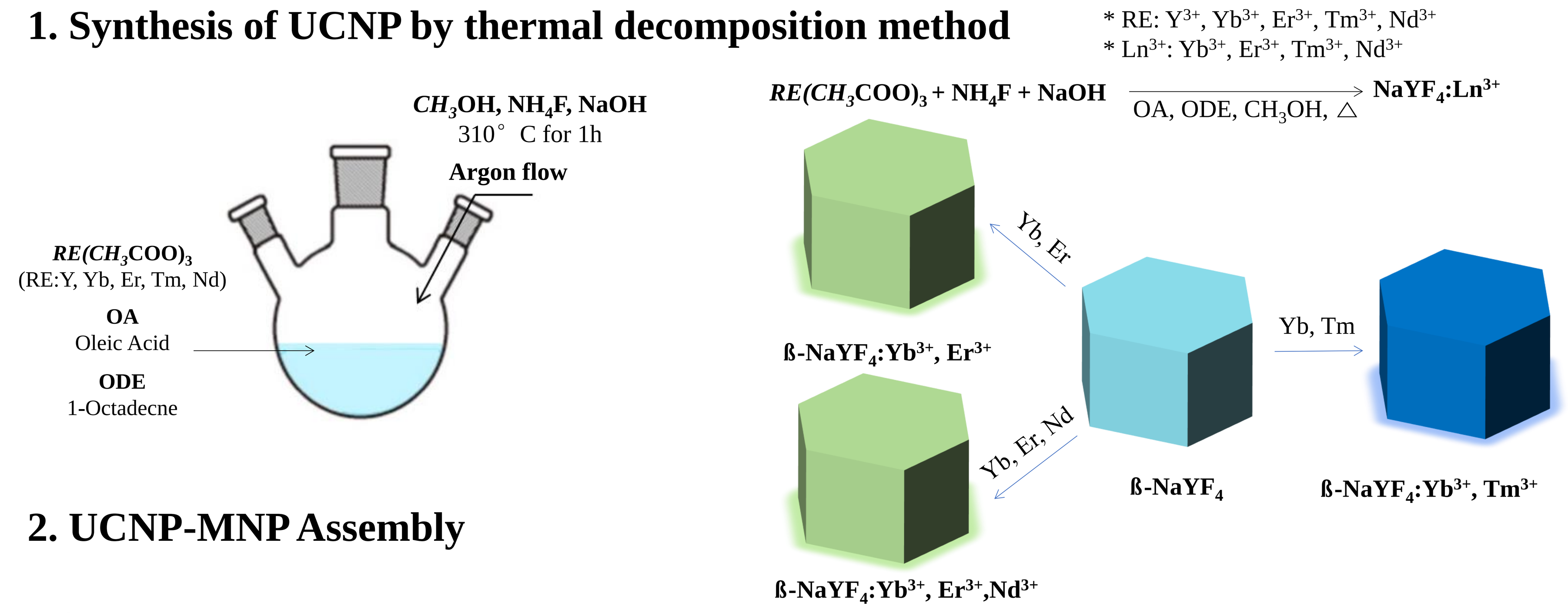
Therefore, tuning photoluminescence property of synthesized UCNPs was carried out by controlling the doping composition of lanthanide ions. We were able to observe the different photoluminescence energy depending on different dopants along with change in intensity with increasing dopant concentration.

For further application, we synthesized multifunctional supernanoparticle by assembling UCNPs with magnetic nanoparticles (MNPs). Both optical and magnetic properties were successfully characterized with uniform shape. Thus, we expect that integrated functions of multifunctional optical-magneto nanoparticles could lead to new opportunities in nano-bio-applications.

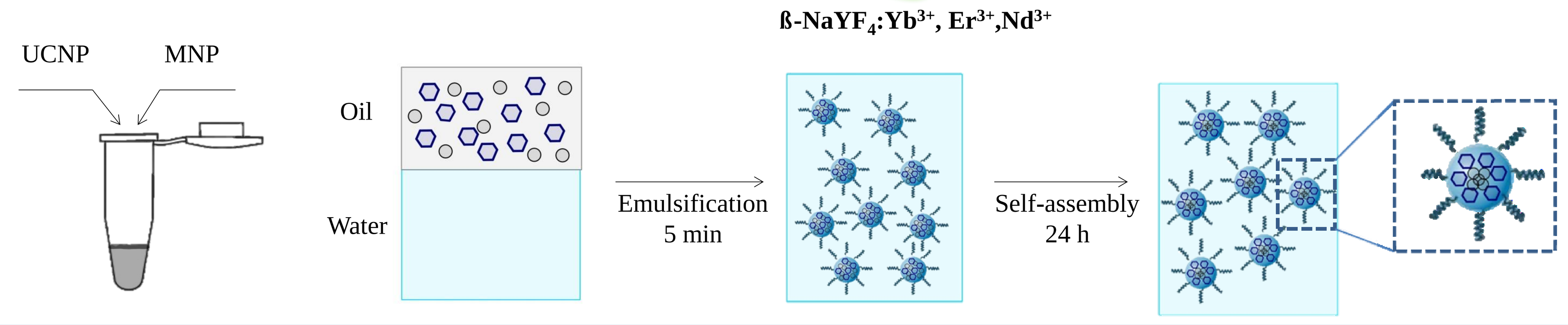
Experimental Methods

1. Synthesis of UCNP by thermal decomposition method

* RE: Y^{3+}, Yb^{3+}, Er^{3+}, Tm^{3+}, Nd^{3+}
* Ln^{3+}: Yb^{3+}, Er^{3+}, Tm^{3+}, Nd^{3+}



2. UCNP-MNP Assembly



Results

1. Monodisperse UCNP with various dopants and concentration

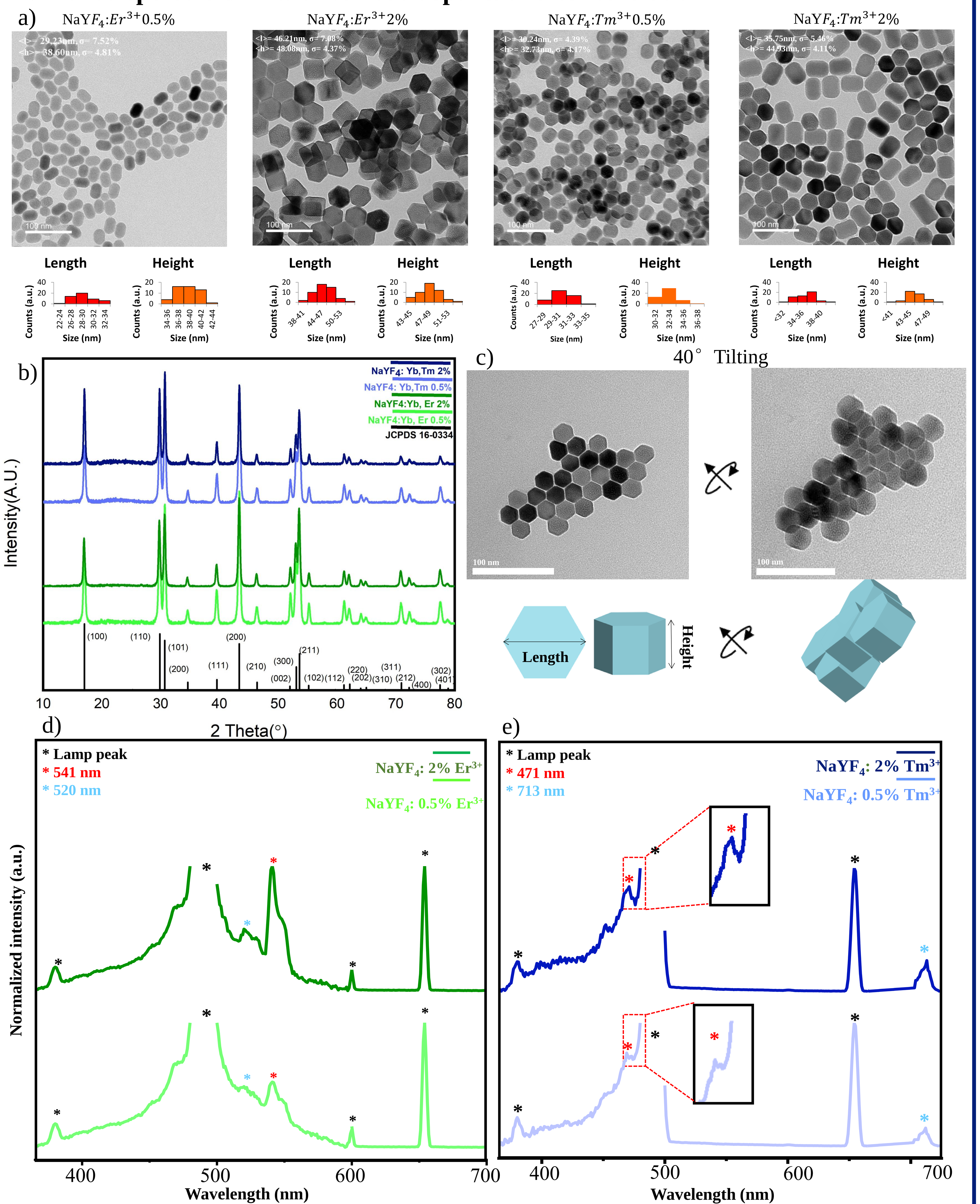
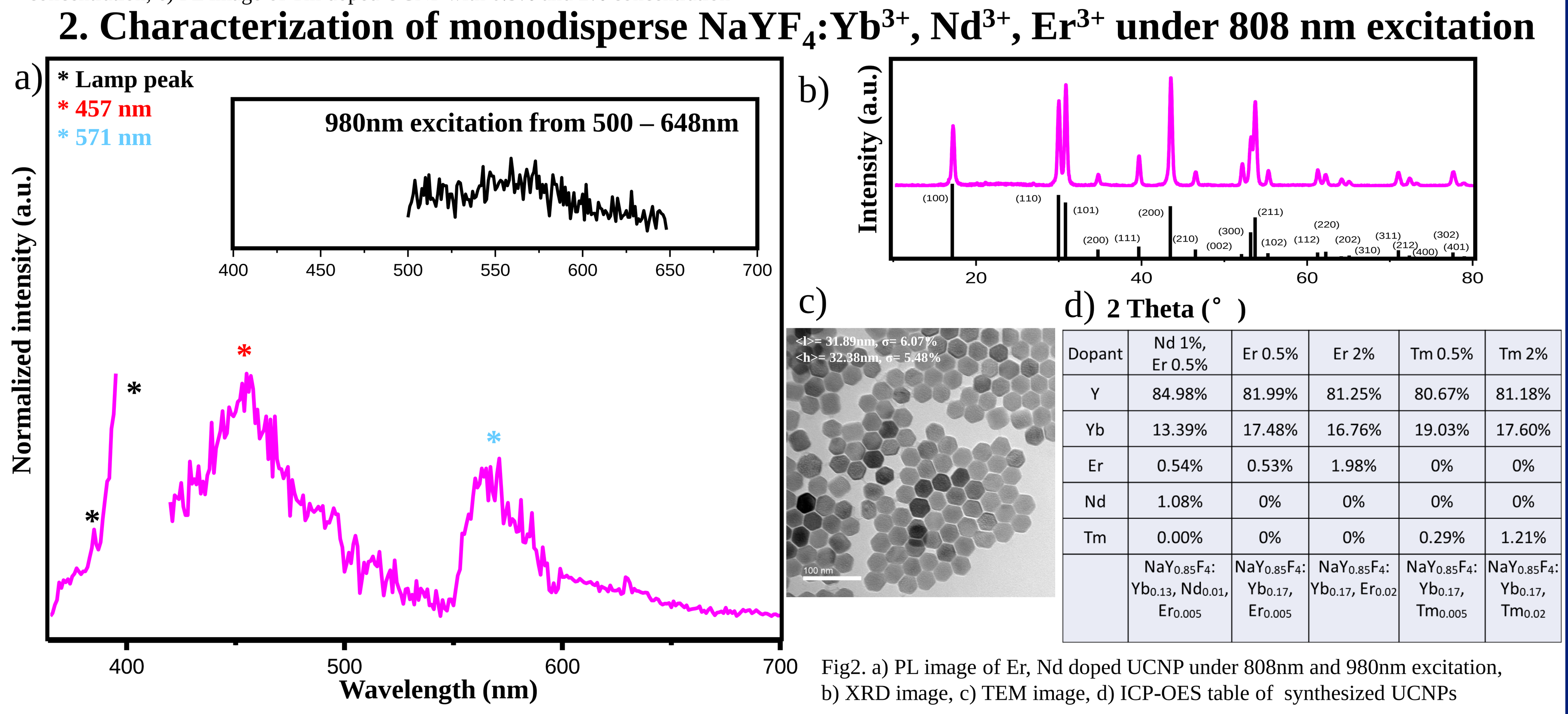


Fig1.a) TEM images of Er and Tm doped UCNP with different concentration, b) XRD image, c) high tilting TEM image, d) PL image of Er doped UCNP with 0.5% and 2% concentration, e) PL image of Tm doped UCNP with 0.5% and 2% concentration

2. Characterization of monodisperse $NaYF_4$:Yb^{3+}, Nd^{3+}, Er^{3+} under 808 nm excitation



d)

Dopant	Nd 1%, Er 0.5%	Er 0.5%	Er 2%	Tm 0.5%	Tm 2%
Y	84.98%	81.99%	81.25%	80.67%	81.18%
Yb	13.39%	17.48%	16.76%	19.03%	17.60%
Er	0.54%	0.53%	1.98%	0%	0%
Nd	1.08%	0%	0%	0%	0%
Tm	0.00%	0%	0%	0.29%	1.21%
	$NaY_{0.85}F_4$: $Yb_{0.13}$, $Nd_{0.01}$, $Er_{0.005}$	$NaY_{0.85}F_4$: $Yb_{0.17}$, $Er_{0.005}$	$NaY_{0.85}F_4$: $Yb_{0.17}$, $Er_{0.02}$	$NaY_{0.85}F_4$: $Yb_{0.17}$, $Tm_{0.005}$	$NaY_{0.85}F_4$: $Yb_{0.17}$, $Tm_{0.02}$

Fig2. a) PL image of Er, Nd doped UCNP under 808nm and 980nm excitation, b) XRD image, c) TEM image, d) ICP-OES table of synthesized UCNPs

3. Characterization of $NaYF_4$:Yb^{3+}, Tm^{3+}- MNP supernanoparticle

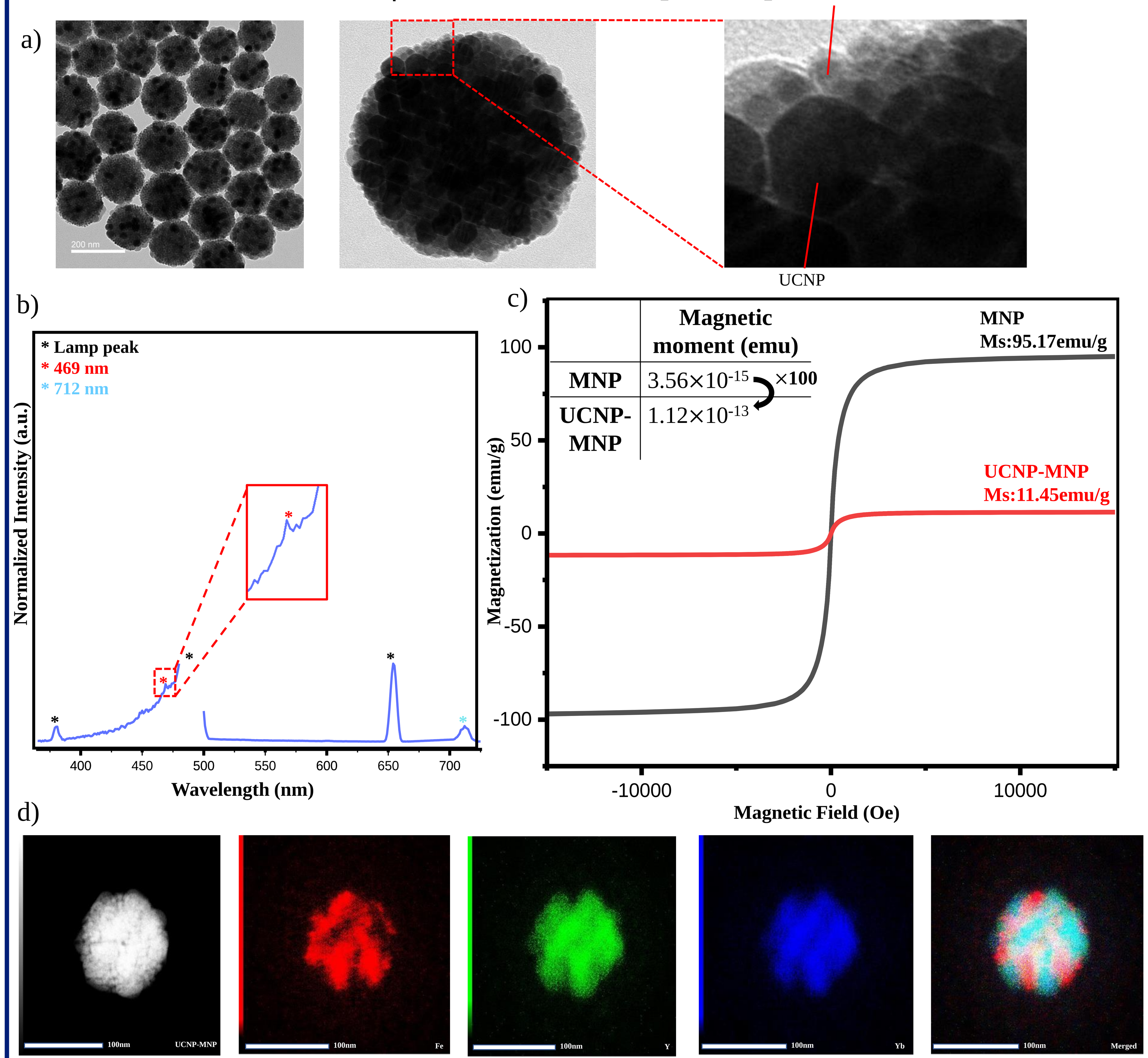


Fig1.a) TEM images of Tm doped UCNP-MNP nanoparticle, b) PL image, c) VSM image, d) EDS image of UCNP-MNP assembly

Conclusion & Further Study

In this study, we were able to synthesize monodisperse hexagonal prism shape UCNPs by varying dopant compositions. Each UCNPs featured distinguished photoluminescence energy in the visible light spectrum along with different intensity depending on dopant species and concentrations. Furthermore, the assembled UCNP-MNP supernanoparticle showed both optical and magnetic properties. We were able to observe similar results for other UCNP-MNP supernanoparticle that were not shown. As a result, synthesized UCNP-MNPs have the potential to serve as a multifunctional nanoparticle capable of activating multiple neurons by both optically and magnetically.

For further studies, controlling the structure of the UCNP-MNP assembly must be considered in order to maximize both optical and magnetic properties. This can be done by forming a core-shell structure, where collective effect can be optimized. Furthermore, applying a uniform magnetic field during the emulsification process could be a solution since MNPs will solely react to the applied field. Lastly, unifying the shapes of both UCNPs and MNPs to 0D spheres will further contribute in forming a monodisperse core-shell structure.

Reference

1. Lee, Song Yeul, et al. "Near-Infrared Light-Triggered Photodynamic Therapy and Apoptosis Using Upconversion Nanoparticles with Dual Photosensitizers." *Frontiers in Bioengineering and Biotechnology*, vol. 8, 16 Apr. 2020
2. Yang, Yuchi, et al. "Scalable Assembly of Crystalline Binary Nanocrystal Superparticles and Their Enhanced Magnetic and Electrochemical Properties." *Journal of the American Chemical Society*, vol. 140, no. 44, 16 Oct. 2018, pp. 15038–15047
3. Liu, Xuan, et al. "Near-Infrared Manipulation of Multiple Neuronal Populations via Trichromatic Upconversion." *Nature Communications*, vol. 12, no. 1, 27 Sept. 2021, p. 5662, www.nature.com/articles/s41467-021-25993-7