Building a near-infrared responsive upconverting nanoplatform against hypoxic tumors via NO-enhanced photodynamic therapy

Ying Lan ${ }^{\text {a }}$, Xiaohui Zhu ${ }^{*}$, Ming Tang ${ }^{\text {a }}$, Yihan Wu ${ }^{\text {a }}$, Jing Zhang ${ }^{\text {a }}$, Jinliang Liu ${ }^{\text {a }}$, Yong Zhang*a, ${ }^{\text {a }}$

1. School of Environmental and Chemical Engineering, Shanghai University, Shanghai, China, 200444
2. Department of Biomedical Engineering, Faculty of Engineering, National University of Singapore, Singapore 117583

Corresponding Author:
*E-mail: xhzhu@shu.edu.cn; biezy@nus.edu.sg.

## Supporting Figure Captions

Figure S1. X-ray diffraction patterns of $\mathrm{NaYF}_{4}: \mathrm{Yb}$ core, $\mathrm{NaYF}_{4}: \mathrm{Yb} @ \mathrm{NaYbF}_{4}: \mathrm{Tm} / \mathrm{Gd}$ core-shell and $\mathrm{NaYF}_{4}: \mathrm{Yb} @ \mathrm{NaYbF}_{4}: \mathrm{Tm} / \mathrm{Gd} @ \mathrm{NaYF}_{4}$ core-shell-shell nanoparticles.

The standard pattern of $\beta-\mathrm{NaYF}_{4}$ (JCPDS $16-0334$ ) is used as a reference.
Figure S2. TEM image and size distribution (inset) of the NaYF4@NaYbF4:Tm@NaYF4 core-shell-shell nanoparticles with varying inner shell thickness. Scale bars for all images are 100 nm .

Figure S3. Comparison of upconversion emission intensity of the core-shell $\mathrm{NaYF}_{4}: \mathrm{Yb} / \mathrm{Tm} @ \mathrm{NaYF}_{4}$ with core-shell-shell $\mathrm{NaYF}_{4} @ \mathrm{NaYbF}_{4}: \mathrm{Tm} @ \mathrm{NaYF}_{4}$ nanoparticles.

Figure S4. Luminescence decay curves of a series of $\mathrm{NaYF}_{4}: \mathrm{x} \% \mathrm{Yb} @ \mathrm{NaYbF}_{4}: 1 \% \mathrm{Tm}, 30 \% \mathrm{Gd} @ \mathrm{NaYF}_{4}(\mathrm{x}=0,15,30,45)$ UCNPs under 980 nm excitation.

Figure S5. Zeta potential of UCNPs $@ \mathrm{mSiO}_{2}$ and UCNPs@ $\mathrm{mSiO}_{2}-\mathrm{NH}_{2}$ in ethanol solution.

Figure S6. UV-Vis absorption spectra of standard curcumin (a) and RBS (b) solution with different concentrations. The calibration curve (concentration vs. absorbance) of solution at 425 nm for (c) curcumin and 350 nm for (d) RBS.

Figure S7. UV-Vis absorption spectra of supernatants of UCNPs @ $\mathrm{mSiO}_{2}$-CUR-RBS collected by centrifugation after they were soaked in deionized water, PBS buffer and cell culture medium (DMEM) for 24 hours.

Figure S8. Representative photographs of segregated tumors after 14 days of PDT treatment.

Figure S9. Standard curve of Griess assay for NO detection.

Figure S1


## Figure S2



Figure S3


Figure S4


Figure S5


Figure S6


Figure S7


Figure S8


Figure S9


