Supporting information

An NIR-driven biosensor based on the metal-enhanced fluorescence effect and a signal amplification strategy for miRNA detection

Dabin Liu^{1,2}, Wenzhang Zhu³, Bin Qiu⁴, Shiqian Zhang^{5*}

1. The First Clinical College of Shandong University, Jinan, 250014, China

2. Department of Gynecology, Fujian Maternity and Child Health Hospital, College of

Clinical Medicine for Obstetrics & Gynecology and Pediatrics, Fujian Medical

University, Fuzhou, 350001, China

3. College of Materials Science and Engineering, Fuzhou University, Fuzhou, 350108,

China

4. College of Chemistry, Fuzhou University, Fuzhou, 350108, China

5. Department of Gynecology, Qilu Hospital of Shandong University, Jinan, 250014,

China



Figure S1 Specific surface areas of the SNs and WSNs



Figure S2 FTIR spectra of WSNs, WSNs-NH $_2$ and WSNs-COOH



Figure S3 FTIR spectra of UCNP (red line) and UCNP@PDA (cyan line)







Figure S5 XPS spectrum of UP/Au



Figure S6 UV-vis spectra of UP before and after AuNP loading

detailed of А analysis the transfer existing in energy NaErF₄:0.5%Tm@NaGdF₄:40%Yb UCNPs reveals that the photon population of the $^4\mathrm{I}_{11/2}$ energy state of a given Er^{3+} can be achieved through direct excitation $({}^{4}I_{15/2} \rightarrow {}^{4}I_{11/2})$ or energy transfer from the ${}^{4}I_{11/2}$ energy state of adjacent Er^{3+} ions. The energy value of the ${}^{3}\text{H}_{5}$ energy state of Tm³⁺ is slightly lower than that of the ${}^{4}\text{I}_{11/2}$ energy state of Er³⁺, enabling the ³H₅ energy state of Tm³⁺ to capture the energy of the ${}^{4}I_{11/2}$ energy state of Er³⁺ and undergo an energy transfer process of ${}^{4}I_{11/2}$ (Er³⁺) $\rightarrow {}^{3}H5$ (Tm^{3+}) , thereby reducing the migration of Er^{3+} energy to surface defects. Subsequently, reverse energy transfer (EBT) occurs from the ³H5 energy state of Tm^{3+} to the ${}^{4}I_{13/2}$ energy state of Er^{3+} , leading to an electron transition to the ${}^{4}F_{9/2}$ state and then back to the ground state, enhancing the red upconversion emission. The Yb³⁺ ions doped in the shell can absorb photons and transition from the ${}^{4}F_{7/2}$ to the ${}^{4}F1_{5/2}$ energy state and then perform two consecutive energy transfers to Er³⁺ (⁴I_{11/2} and ${}^{4}F_{7/2}$), thereby enhancing the radiative electron transition of Er^{3+} and promoting red and green light emission. The ${}^{2}F_{15/2}$ energy level of Yb³⁺ is almost at the same level as the ${}^{4}I_{11/2}$ energy level of Er³⁺. After Yb³⁺ absorbs photons and reaches the ${}^{4}F_{15/2}$ energy state, it preferentially transfers energy to the ${}^{4}I_{11/2}$ energy level of Er^{3+} (mainly Er^{3+} at the core-shell interface). A part of the energy released by Er^{3+} in the ${}^{4}I_{11/2}$ excited state is captured by the ³H₅ energy state of Tm³⁺, and then a BET process of Tm³⁺ (³H₅) \rightarrow Er³⁺ (⁴I_{13/2}) occurs, exciting Er³⁺ to transition to the ⁴F_{9/2} energy state. The result reveal that UCNP has bright red fluorescence at 655 nm.



Figure S7 Schematic diagram of energy transfer inside the core-shell UCNPs (black solid arrows, red arrows, blue arrows, and wine red arrows represent photon excitation, energy transfer, and radiation emission, respectively)



Figure S8 Stability of UP/Au-ssDNA2. The quenching efficiency was calculated via the formula $(F-F_0)/F$, where F_0 and F represent the fluorescence values of the system

before and after ssDNA2 was added, respectively.