Supporting Information

Significant enhancement of photon upconversion of a single fluorescent microsphere via annular near-field Localization

Chuangxin Wu,[#a] Jiujie Zeng,[#a] Guozheng Nie,[a] Shiping Zhan,*[b]Xiaofeng Wu,[b] Yunxin Liu,*[a]

a: Department of Physics and Electronic Science, Hunan University of Science and Technology, Xiangtan, 411201, China.

b: School of Mechatronic Engineering and Automation, Foshan University, Foshan, 528000, P.R China

# Contributed equally.

* Corresponding author: spzhan86@163.com, and lyunxin@163.com
ORCID：ORCID: 0000-0003-1333- 4619.

1. Experimental

1.1 Materials

Yttrium oxide (99%), gadolinium oxide (99.99%), ytterbium oxide (99.99%) and erbium oxide (99%), sodium hydroxide (NaOH, AR), hydrochloric acid (HCl, AR), ammonium fluoride (NH_4F, AR), methanol (AR), ethanol (AR), oleic acid (OA, AR), octadecene (ODE, AR), were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China) and Sigma Aldrich Co. Polystyrene (PS) microspheres with the diameter of 5μm in aqueous solution (10 wt%) were purchased from Goose (Tianjin)

Technology Co. Gold spheres with the diameter of 5μm were purchased from Suzhou Micro-Nano Technology Co.

1.2 Preparation of core-shell nanocrystals NaGdF4:Yb,Er@NaYF4

Three-necked flasks (B1) (B2) were added with NaOH/ NH_4F solution, OA, ODE respectively, warmed up to 80°C and stirred for 1.5h and set aside. Three-necked flask (A1) add YCl_3, $YbCl_3$, $ErCl_3$, OA, heating to 160 ℃, reaction 1h after the addition of ODE, reaction 20min after cooling down to 60 ℃ add beaker (B1) solution stirring for 20min standby; three-necked flask (A2) add YCl_3, OA, heating to 160 ℃, reaction 1h after the addition of ODE, reaction 20min after cooling down to 60 ℃ add (B2) solution stirring for 20min standby. Add (B2) solution at 60 ℃ and stir for 20 min. Three-necked flask (C) add ODE, OA nitrogen environment heating to 310 ℃, after the temperature is stabilized add the solution in the three-necked flask (A1), the reaction 0.5h, then add the solution in (A2), the reaction 0.5h, cooling down to 60 ℃, centrifugation, centrifugal dispersed in 6 ml of cyclohexane to obtain the NaGdF4:18%Yb2%Er@$NaYF_4$ nanoparticle Solution.

1.3 Preparation of ligand-free nanoparticles

UCNPs with the surface ligand oleic acid was dispersed in 20 μL of hydrochloric acid solution and sonicated for 15 min to remove the surface ligand. After the reaction, the nanoparticles were collected by centrifugation at 10,000 rpm for 5 min. The resulting product was washed several times with ethanol and deionized water and then re-dispersed in deionized water and set aside.

1.4 Preparation of PS microspheres coated with UCNPs (PS@UCNPs)

The ligand-free nanoparticle solution was added to a mixture of PS microsphere dispersion (5 μL) and butanol (200 μL). The mixture was ultrasonicated and kept at room temperature for 30 min, then centrifuged at 4000 rpm for 5 min, washed with deionized water, and finally redispersed in deionized water.

1.5 Controlled Arrangement of Microspheres

The microspheres are grasped, moved and released by the tip of a SiO_2 micro-probe equipped on a micro-manipulation platform with the aid of an optical microscope. Grasping and releasing microspheres are controlled by the surface strain of the SiO_2 micro-probe.

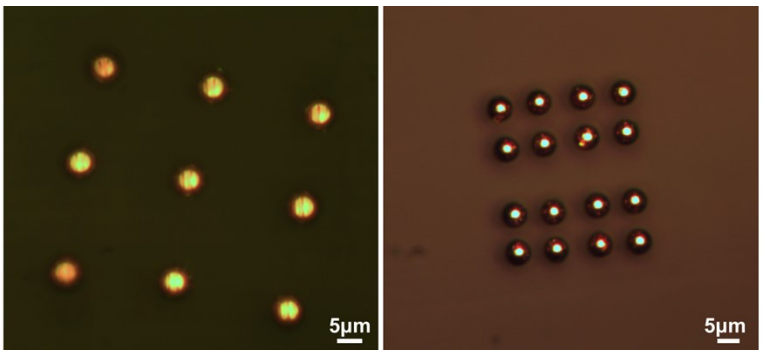

Fig 1 Array of regularized gold spheres

1.6 Characterization

The morphology and particle size of the prepared nanocrystals were examined by JEOL 2100 transmission electron microscope (TEM) at an accelerating voltage of 200 kV. The microspheres were measured using a Nova Nano SEM 450 scanning electron microscope (SEM) and Fluorescence microscope Olympus BX43. Upconversion luminescence spectra were recorded on an F-2700 fluorescence spectrometer

combined with a near-infrared (NIR) 980 nm laser as the pump power. The simulations were calculated using the Finite-Difference Time-Domain (FDTD) method.

1.7 FDTD calculation conditions

The material of the sphere is Au, with a diameter of 5 μm. We use PS microspheres with a refractive index of 1.6 directly above the gold sphere, add several point light sources on the surface of the PS microspheres to replace the UCNPs, and add a local field strength monitor in the x y plane at the center of the circle of the PS sphere, through which we get our simulation results.

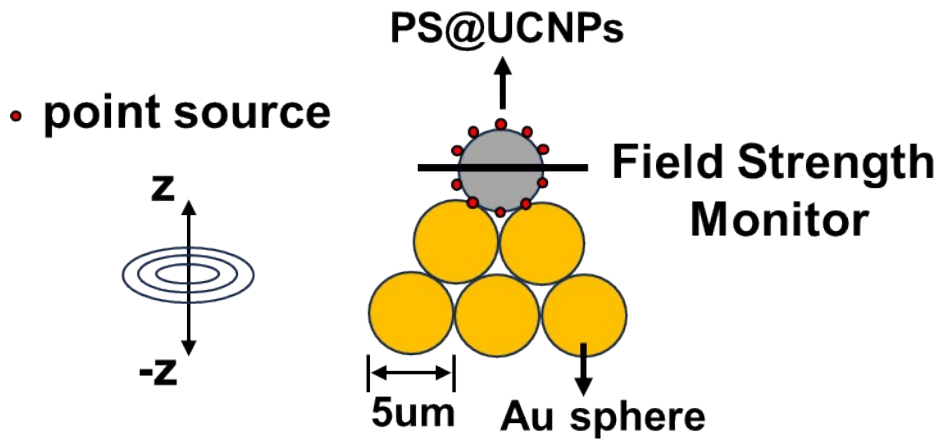

Fig 2 FDTD computational model

1.8 microcavity extinction coefficient

Microcavity extinction coefficient: We design different microsphere models and place them in different calculation areas. Parallel light with the wavelength of 300 nm ~ 1000 nm is added to directly radiate the microsphere model, and spectral monitors are added above and below the model and parallel light, which are counted as monitor

1 and monitor 2 separate detection of reflected and transmitted light. The calculation result is: （| Plane wave | - | monitor 1 | - | monitor 2 | ）/| Plane wave |= model extinction coefficients.

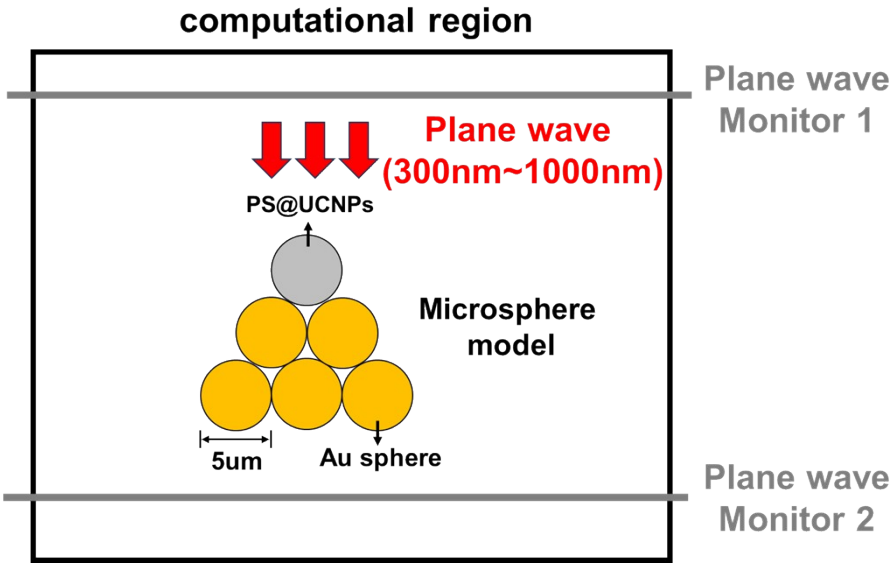

Fig 3 microcavity extinction coefficient computational model