Electronic supplementary information

Surface plasmon resonance enhanced upconversion luminescence in aqueous media for TNT selective detection

Nina Tu and Leyu Wang*

State Key Laboratory of Chemical Resource Engineering, School of Science, Beijing University of Chemical Technology, Beijing 100029, China

Fax and Tel: (+86-10-64427869), E-mail: lywang@mail.buct.edu.cn

Chemicals and reagents

2,4,6-trinitrotoluene (TNT) and 2,4,6-trinitrophenol (TNP) were provided by National Security Department of China and recrystallized with ethanol before use. 2,4-dinitrotoluene (DNT) and nitrobenzene (NB) were purchased from Aladdin Chemistry Co., Ltd. (China) and used without further purification. In addition, all of the explosives should be used with extreme caution and must be kept away from fire, striking and friction. The four nitroaromatics were respectively dissolved in the mixed solvent of acetonitrile and ethanol (volume ratio of 1:4) to obtain the stock solution before use. In short, the stock solution with a concentration of 0.2 mg mL^{-1} was prepared by dissolving 6 mg of nitroaromatics in 30 mL of mixed solvent containing acetonitrile (6 mL) and ethanol (24 mL). The work solution with the concentration of 0.02 mg mL^{-1} was obtained by diluting 2 mL of the stock solution with 18 mL of methanol. All other chemicals were analytical grade and used as received. Deionized (DI) water was used throughout. Oleic acid, oleylamine, sodium stearate, 1-octadecene, and hydrofluoric acid were purchased from Aldrich. All rare-earth nitrates used in this work were purchased from Beijing Ouhe Chemical Reagent Co. The poly-succinimide was obtained from Shijiazhuang Desai Chemical Company. Cysteamine was purchased from Biological Science and Technology Co. Mercapto-ended poly (ethylene glycol) (SH-mPEG, Mw = 5000) was purchased from Beijing Kaizheng Biological Engineering Development Co. NaOH, ethanol, acetonitrile, methanol, *N*, *N*-dimethylformamide, cyclohexane, chloroform and $HAuCl_4 \cdot 2H_2O$ were purchased from Beijing Chemical Factory (China).

Characterization

The size and morphology of the nanomaterials were characterized by a JEM-1200 EX transmission electron microscope (TEM) (JEOL). The upconversion emission spectra were performed on an F-4600 fluorospectrometer (Hitachi) equipped with a 980 nm diode laser. Dynamic light scattering (DLS) particle size analysis was carried out on a Malvern Master 2000 ζ and size analyzer. The absorption spectra were conducted on a UNICO 2802PC spectrophotometer with a spectral window range of 300−700 nm.

Synthesis of hydrophobic $NaYF_4$:Yb^{3+}/Er^{3+} nanoparticles[S1]

0.35 g of sodium stearate, 7 mL of oleic acid and 8 mL of octadecene were added into a three-necked flask. Under stirring, 4 mL of the rare-earth oleate solution and 1.4 mL of the HF–oleylamine solution were injected into the flask and kept at 80 °C for 20 minutes. Then the solution was kept at 180 °C for 10 minutes. Afterwards, it was heated to 310 °C and kept at 310 °C for 1 hour. The mixture solution was kept under a protective nitrogen flow throughout. The final reaction solution was cooled to room temperature and the product was collected by washing with cyclohexane and ethanol, centrifugation for three times and finally dispersed in 4 mL of chloroform for later use.

Synthesis of hydrophilic $NaYF_4$:Yb^{3+}/Er^{3+} nanoflowers

First of all, oleylamine functionalized polysuccinimide was prepared. In brief, 0.8 g of polysuccinimide was dissolved in 15 mL of *N, N*-dimethylformamide, 0.8 mL of oleylamine was added under magnetic stirring. The mixture was then treated at 100 °C for 6 h. The oleylamine functionalized polysuccinimide was collected by precipitation with methanol and finally dispersed in chloroform (8 mL). The hydrophilic $NaYF_4$:Yb^{3+}/Er^{3+} nanoflowers were synthesized as follows. Typically, 1.0 mL of chloroform solution containing oleylamine functionalized polysuccinimide (60 mg mL^{-1}) and $NaYF_4$:Yb^{3+}/Er^{3+} nanoparticles (10.0 mg mL^{-1}) was added into 10 mL of NaOH (30 mM) solution under ultrasonication (8 min) and then stirred at 55 °C for 1.5 h to remove the chloroform by evaporation. The hydrophilic nanoflowers were collected by centrifugation and dispersed into deionized water (10 mL).

Synthesis of amine-functionalized gold nanoparticles (Au NPs)

Gold nanoparticles were first prepared as follows. In brief, 1.0 mL of cysteamine (6.5 mM) was added to 40 mL of boiling water containing $HAuCl_4$ (2.0 mg) under magnetic stirring. The solution was kept boiling for 10 min till the colour turned from yellowish to magenta. In order to improve the stability of the as-synthesized Au NPs, 1.0 mg of SH-mPEG was added finally. The Au NPs were collected by centrifugation and then redispersed into water (7 mL).

2,4,6-trinitrotoluene (TNT) analysis

Briefly, the $NaYF_4$:Yb^{3+}/Er^{3+} nanoflowers (0.1 mg mL^{-1}) were mixed with gold nanoparticles (38 μg mL^{-1}) and various concentrations of TNT. Subsequently, the mixed solution was diluted to 1.0 mL with NaH_2PO_4–Na_2HPO_4 (pH 7.0, 0.02 mol L^{-1}) phosphate buffer solution (PBS). The upconversion emission spectra of the mixture solution were collected under irradiation with a 980 nm diode laser.

Supporting References:

S1. M. L. Deng, Y. X. Ma, S. Huang, G. F. Hu and L. Y. Wang, *Nano Res.*, 2011, **4**, 685-694.

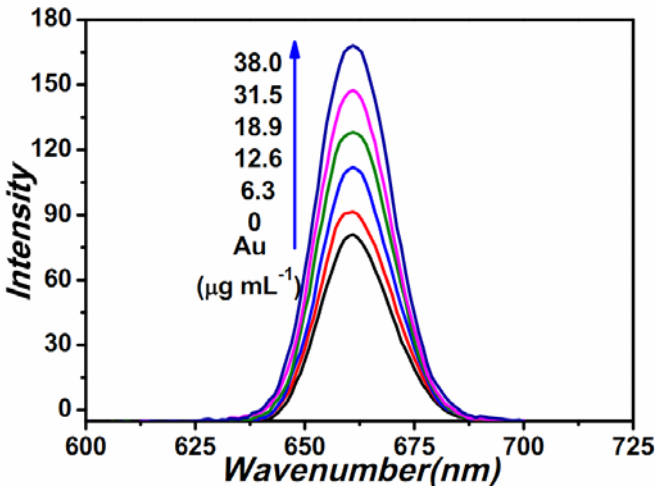

Fig. S1 Effects of gold NPs (Au) concentrations on the enhancement of UC luminescence of $NaYF_4$ nanoflowers (0.1 mg mL^{-1}) in the absence of TNT.

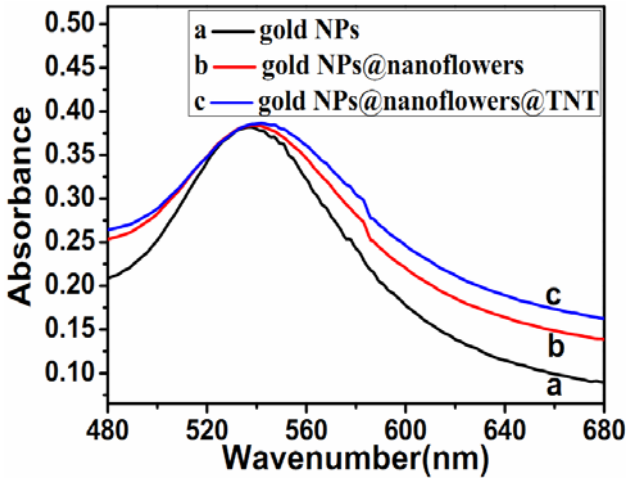

Fig. S2 UV−visible absorption spectra of the three mixture solutions. (a) gold NPs (38 μg mL^{-1}); (b) gold NPs (38 μg mL^{-1}) + $NaYF_4$ nanoflowers (0.1 mg mL^{-1}); (c) gold NPs (38 μg mL^{-1}) + $NaYF_4$ nanoflowers (0.1 mg mL^{-1}) + TNT (4.0 μg mL^{-1}).

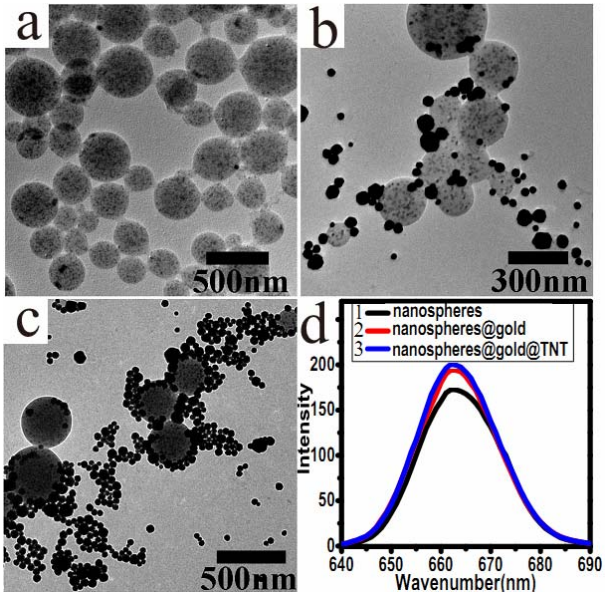

Fig. S3 TEM images (a, b and c) and upconversion luminescence spectra (d) of hydrophilic $NaYF_4$ nanospheres (a and d1); hydrophilic $NaYF_4$ nanospheres + gold NPs (38 μg mL^{-1}) (b and d2); hydrophilic $NaYF_4$ nanospheres (0.1 mg mL^{-1}) + gold NPs (38 μg mL^{-1}) + TNT (8 μg mL^{-1}) (c and d3), respectively.

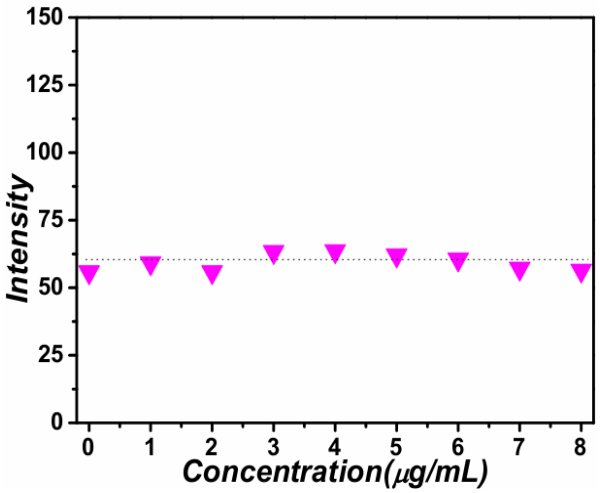

Fig. S4 Influence of TNT on the UC luminescence of $NaYF_4$ nanoflowers (0.1 mg mL^{-1}) in the absence of gold NPs.

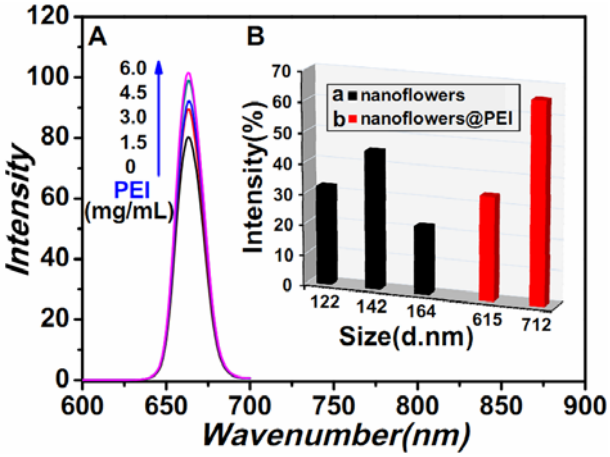

Fig. S5 (A) Effects of polyetherimide (PEI) with different concentrations on the UC luminescence of $NaYF_4$ nanoflowers (0.1 mg mL^{-1}). (B) Size distribution profiles by dynamic light scattering (DLS) (a) $NaYF_4$ nanoflowers (0.1 mg mL^{-1}); (b) $NaYF_4$ nanoflowers (0.1 mg mL^{-1}) + PEI (6 mg mL^{-1}).

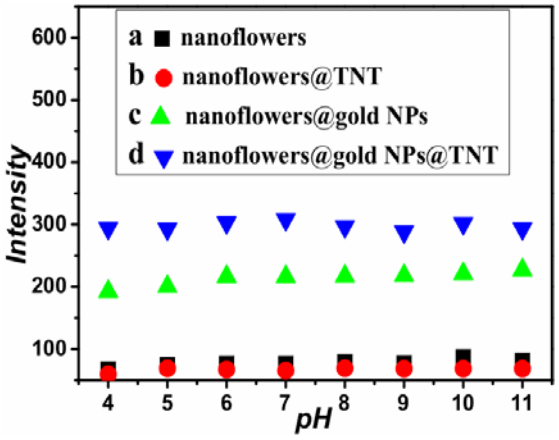

Fig. S6 Effects of pH on the UC luminescence of the mixture solutions. (a) only $NaYF_4$ nanoflowers (0.1 mg mL^{-1}). (b) $NaYF_4$ nanoflowers (0.1 mg mL^{-1}) + TNT (4.0 μg mL^{-1}). (c) $NaYF_4$ nanoflowers (0.1 mg mL^{-1}) + gold NPs (38 μg mL^{-1}). (d) $NaYF_4$ nanoflowers (0.1 mg mL^{-1}) + gold NPs (38 μg mL^{-1}) + TNT (4.0 μg mL^{-1}). Buffer solution and concentration, pH (4, 5): CH_3COOH−CH_3COONa (0.02 mol L^{-1}); pH (6−8): NaH_2PO_4−Na_2HPO_4 (0.02 mol L^{-1}); pH (9−11): Na_2CO_3−$NaHCO_3$−NaOH (0.02 mol L^{-1}).

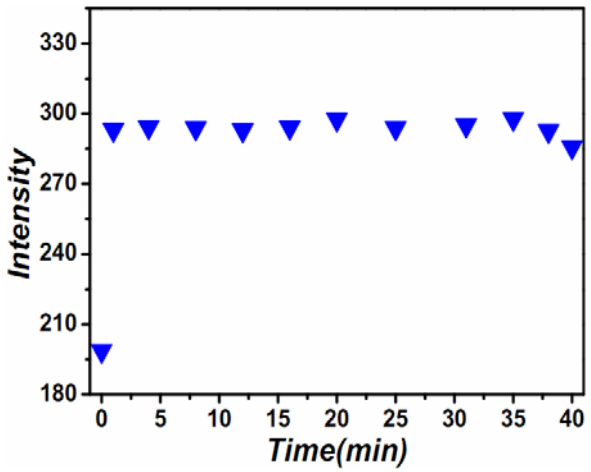

Fig. S7 Influence of the incubation time on the UC luminescence enhancement between the $NaYF_4:Yb^{3+}/Er^{3+}$ nanoflowers (0.1 mg mL^{-1}), gold NPs (38 μg mL^{-1}) and TNT (4.0 μg mL^{-1}). Buffer solution: NaH_2PO_4–Na_2HPO_4 (pH 7.0, 0.02 mol L^{-1}).

Table S1. Detection of trace TNT in mixed water samples [a]

sample	Concentration (μg mL^{-1})		recovery (%)
	taken	found (mean, n = 6)	
TNT/TNP	4.0/2.0	4.03±0.03	100.8±0.75
TNT/DNT	4.0/2.0	3.98±0.06	99.50±1.50
TNT/NB	4.0/2.0	4.02±0.05	100.5±1.25
TNT/TNP/DNT/NB	4.0/2.0/2.0/2.0	4.08±0.07	102.0±1.75

[a] n is the repetitive measurement number.