Supporting Information

Luminescent Nanoprobes based on Upconversion Nanoparticles and Single-Walled Carbon Nanohorns or Graphene Oxide for Detection of Pb^{2+} ion

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Experimental

1. Materials

All the chemicals were used without further purification: $YCl_3 \cdot 6H_2O$ (99.99%), $YbCl_3 \cdot 6H_2O$ (99.99%), and $ErCl_3 \cdot 6H_2O$ (99.99%) were purchased from Sigma Aldrich. Oleic acid (90%, technical grade), N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC, 98%), N-Hydroxysuccinimide (NHS, 98%), and sodium citrate (anhydrous, 99%) were purchased from Sigma Aldrich. 1-octadecene (>90%, gas chromatography), methanol (99.5%), diethylene glycol (>98%, gas chromatography), ammonium fluoride (guaranteed reagent, 98%), and sodium hydroxide (guaranteed reagent, 97%, flakes) were purchased from Aladin Company. Acetone (99.5%, analytical reagent), cyclohexane (99.5%, analytical reagent), anhydrous ethanol (99.7%, analytical reagent), toluene (99.5%, analytical reagent), chloroform (analytical reagent), lead nitrate, and other metal salts were obtained from Sinopharm Chemical Reagent Co., Ltd. Single-walled carbon nanohorns (JCSCH-95-90-15n, 95%) (SWCNHs) and graphene oxide (JCGO-99-1-2, >99%) (GO) were purchased from Nanjing Jcnano Tech Co., Ltd. Probe DNA (5'-NH_2-$(CH_2)_6$-

GGGTGGGTGGGTGGGT-3'), named as pDNA, was purchased from Sangon Biotech (Shanghai) Co., Ltd. Deionized water was used to prepare all aqueous solutions.

2. **Instrumentation**

The size and morphology of nanoparticles were measured by using a JEM-200CX transmission electron microscope operated at 120 kV and 200 kV using a JEM-2010F high-resolution transmission electron microscope. The crystal phase of UCNPs was identified by X-ray diffraction (XRD) measurements carried out on a 18KW D/MAX2500V PC diffractometer using Cu Kα (λ = 1.54 Å) radiation with 2θ range from 10º to 90º at a scanning rate of 8 º/min. Fourier transform infrared spectroscopy (FT-IR) spectra were acquired in the spectral range from 4000 to 400 cm^{-1} with an Avatar 370 by using pressed KBr pellet technique. The upconversion luminescence (UCL) spectra were obtained on an Edinburgh LFS-920 fluorescence spectrometer equipped with an external 0–800 mW 980 nm adjustable CW laser. The Z-potential measurements of the nanoparticles were performed at 25 °C using a ZETASIZER 3000HS instrument (Malvern Instruments, U.K.).

3. Attachment of the pDNA sequence to the Cit-UCNPs nanoparticles. (Cit-UCNPs-pDNA)

The synthesis of $NaYF_4$:20%Yb,2%Er, $NaYF_4$:Yb,Er@$NaYF_4$ nanoparticles (UCNPs), and citrate-capped UCNPs (Cit-UCNPs) were according to our previously reported method.[1] The pDNA was covalently attached to the surface of the Cit-UCNPs by the carbodiimide coupling reaction. To activate the surface carboxylic acid group, 2 mg of EDC and 3 mg of NHS were firstly added to 1 mL of water containing 1 mg of Cit-UCNPs and the mixture stirred for 2 h at 4 ºC. The precipitates were collected by centrifugation (10,000 rpm, 15 min) and washed three times with deionized water to remove the excess EDC and NHS, and then 1 mL of H_2O containing 20 μL of pDNA (100 μM) was added and the solution was stirred for 10 h at 4 ºC. The Cit-UCNPs-pDNA were obtained by centrifugation and washing with deionized water three times to remove free pDNA. The final products were stored in water at 4 °C for further use, denoted as Cit-UCNPs-pDNA.

4. Syntheses of Cit-UCNPs-pDNA-SWCNHs and Cit-UCNPs-pDNA-GO

For the luminescence quenching experiments, the single-walled carbon nanohorns (SWCNHs) stock solution (0-7.0 μg/mL) were individually added to Cit-UCNPs-pDNA solution (0.3 mg/mL) by using a micropipette and incubated for 60 min at 4 ºC, and the Cit-UCNPs-pDNA-SWCNHs were obtained. Then upconversion luminescence measurements were performed with an external 980 nm laser as the excitation source. Considering the quenching effect, for the subsequent experiments, the

7.0 μg/mL SWCNHs were selected to synthesize the final Cit-UCNPs-pDNA-SWCNHs.

The synthesis of final Cit-UCNPs-pDNA-GO was performed following the similar procedure of Cit-UCNPs-pDNA-SWCNHs except for the 7.0 μg/mL SWCNHs being replaced by 7.0 μg/mL GO.

5. Procedures for Pb^{2+} detection

Lead nitrate (0.02 M) was used for the Pb^{2+}-sensitivity studies, other metal ions, including Fe^{3+}, Fe^{2+}, Mg^{2+}, Ba^{2+}, Ca^{2+}, Na^{+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, and Co^{2+}, were prepared at a concentration of 0.1 M. For selectivity experiments, the test samples were prepared by adding appropriate amounts of metal ions solution to 2.0 mL Cit-UCNPs-pDNA-SWCNHs. For titration experiments, the Pb^{2+} stock solution was added to 2.0 mL Cit-UCNPs-pDNA-SWCNHs solution by using a micropipette, and then UCL spectra were recorded. For competition experiments, Pb^{2+} was added to the solutions containing Cit-UCNPs-pDNA-SWCNHs and other metal ions (Fe^{3+}, Fe^{2+}, Mg^{2+}, Ba^{2+}, Ca^{2+}, Na^{+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, and Co^{2+}) of interest. Subsequently, the upconversion luminescence measurements were carried out under the excitation of 980 nm. The experiments of Cit-UCNPs-pDNA-GO for detection of Pb^{2+} ion were performed with the similar procedures. The LOD was calculated by the equation of $LOD=3S_0/S$, where 3 is the factor at the 99% confidence level, S_0 is the standard deviation of the blank measurements (n = 10), and S is the slope of the calibration curve.

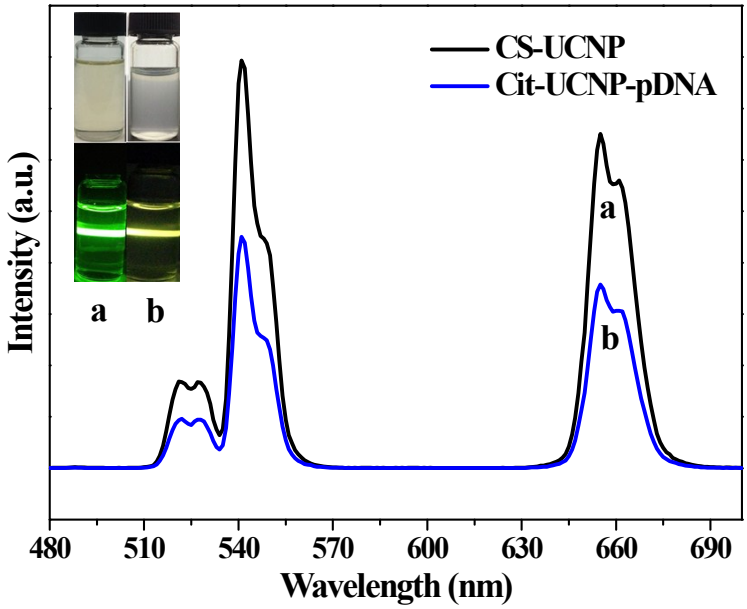

Fig. S1. Upconversion luminescence spectra of (a) $NaYF_4$:Yb,Er@$NaYF_4$ nanoparticles (UCNPs) in cyclohexane and (b) Cit-UCNPs-pDNA in deionized water. The inset shows photographs of the upconversion emission of the corresponding solutions in the daylight (top) and in the dark (bottom) under excitation of 980 nm laser.

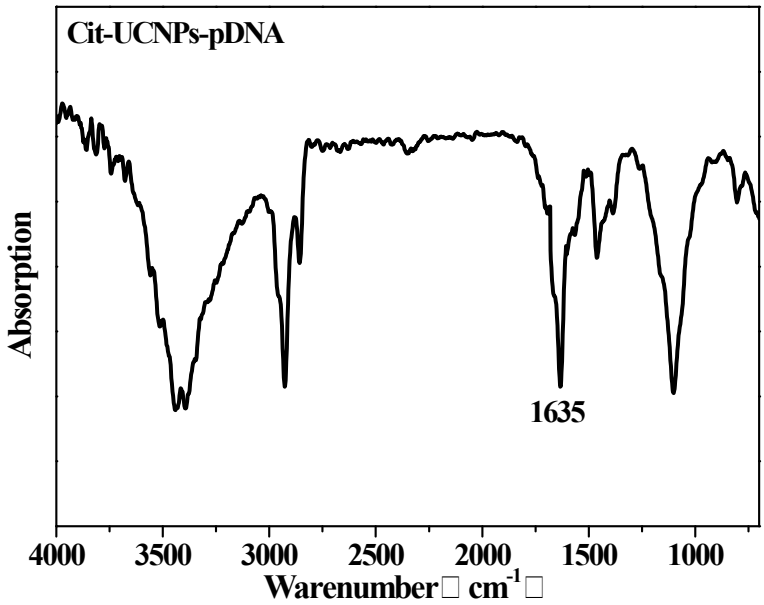

Fig. S2. FT-IR spectrum of Cit-UCNPs-pDNA in water.

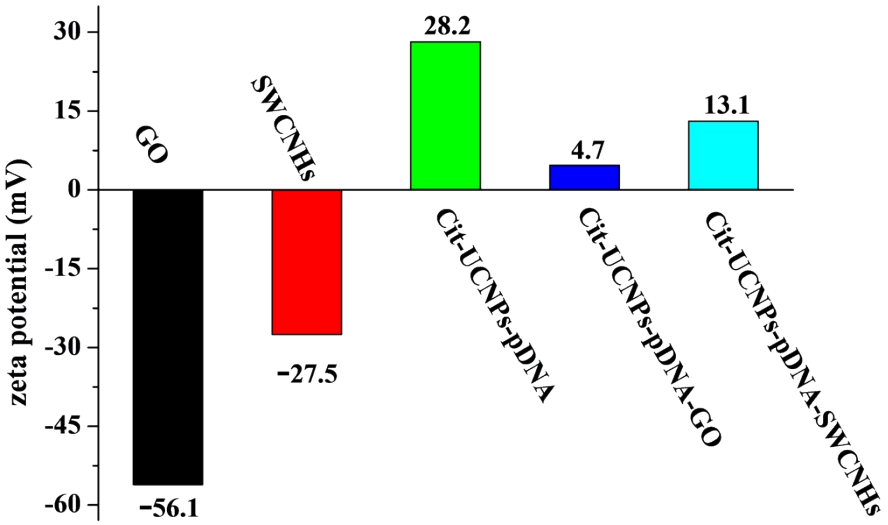

Fig. S3. The zeta potential of GO, SWCNHs, Cit-UCNPs-pDNA, Cit-UCNPs-pDNA-GO, and Cit-UCNPs-pDNA-SWCNHs in water.

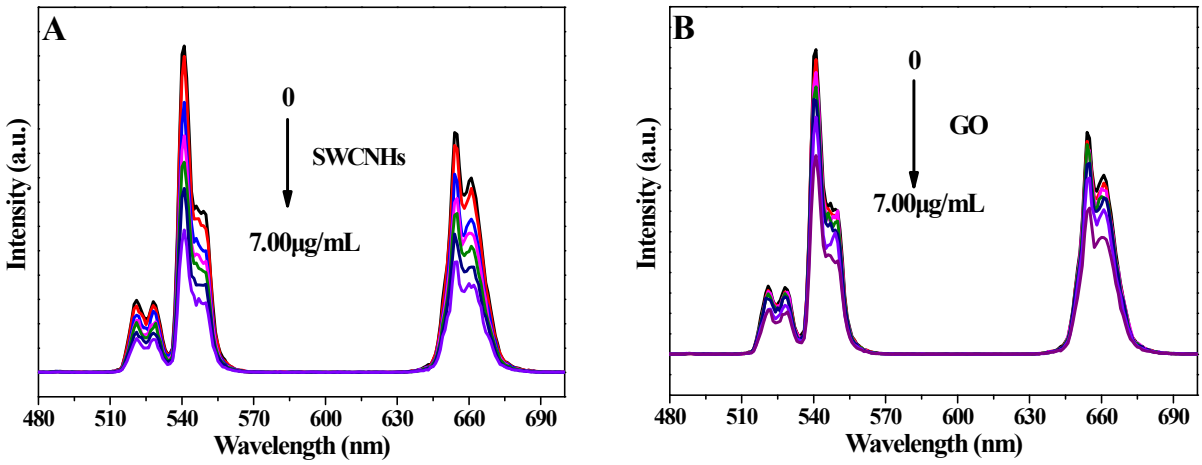

Fig. S4. Upconversion luminescence spectra of Cit-UCNPs–pDNA after incubation with various concentrations of SWCNHs (A) and GO (B). The concentrations of Cit-UCNPs-pDNA is 0.3 mg/mL, the concentrations of SWCNHs and GO are ranged from 0 to 7.0 μg/mL, λ_{ex} = 980 nm.

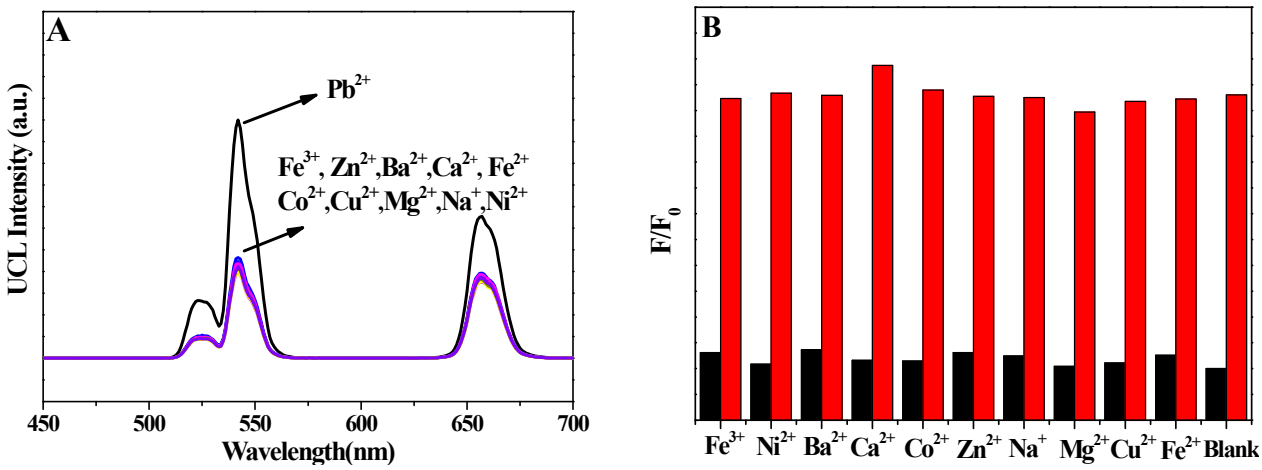

Fig. S5. (A) The UCL spectra of the Cit-UCNPs-pDNA-GO and under the addition of different metal ions; (B) luminescence intensity ratio of Cit-UCNPs-pDNA-GO towards various cations (1.0 μM). Black bars represent the luminescence response of Cit-UCNPs-pDNA-GO towards the metal ions of interest. Red bars represent the subsequent addition of 1.0 μM Pb^{2+} to above solutions (F_0: the emission intensity at 545 nm of Cit-UCNPs-pDNA-GO, and F: the emission intensity at 545 nm of Cit-UCNPs-pDNA-GO towards the metal ions of interest.).

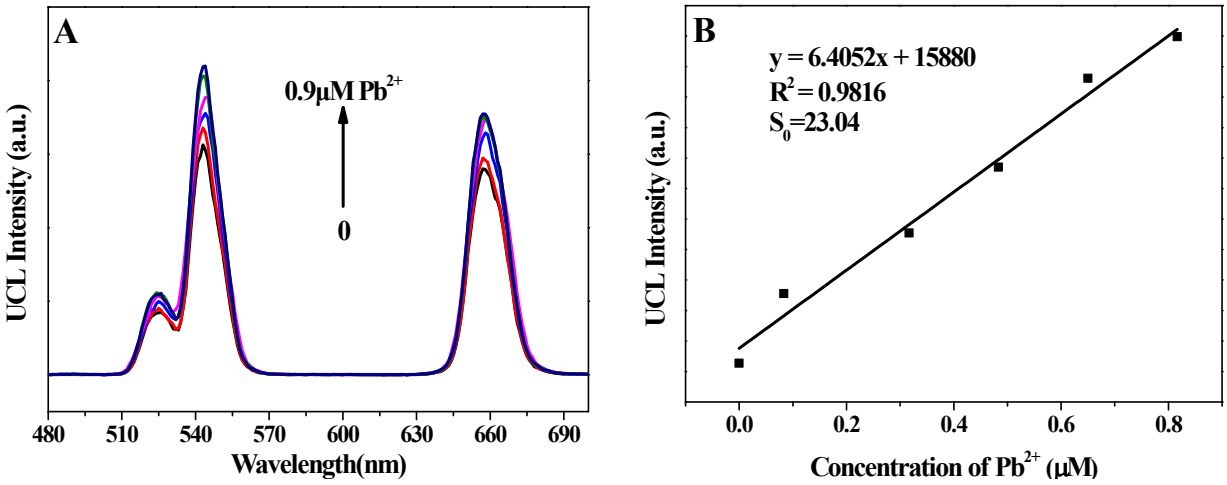

Fig. S6. (A) The UCL spectra of Cit-UCNPs–pDNA-GO nanoprobe under addition of different concentrations of Pb^{2+}. (B) Linear relationship of upconversion luminescence intensity recorded (at 545 nm) versus Pb^{2+} concentration. Pb^{2+} concentration is in the range of 0 to 0.9 μM.

Reference

1. Y. X. Xu, X. F. Meng, J. L. Liu, S. Y. Zhu, L. N. Sun, and L. Y. Shi, *RSC Adv.*, 2015, **6**, 1037.