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Supporting Information

Upconversion nanocrystal 'armoured' silica fibres with superior photoluminescence for miRNA detection

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Experimental Details

Materials

Tetraethyl orthosilicate (TEOS, A.R.), sodium chloride (NaCl, A.R.), ethylene glycol (EG, A.R.) and N-hydroxy-succinimide (NHS, 97.0–102.0%) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Polyvinyl alcohol (PVA, Mw = 88 000), 1-ethyl-3-(3-dimethylaminopropy) carbodiimide (EDC, 98.0%) and phosphoric acid (H_3PO_4, $\geq$ 85 wt%) were purchased from Aladdin Reagents (Shanghai, China). Polyethylenimine, branched (PEI, M_w = 25 000) were acquired from Sigma-Aldrich (St. Louis, MO, USA). Yttrium chloride hexahydrate ($YCl_3 \cdot 6H_2O$, 99.99%), ytterbium(III) chloride hexahydrate ($YbCl_3 \cdot 6H_2O$, 99.9%), erbium chloride hexahydrate ($YbCl_3 \cdot 6H_2O$, 99.5%) and ammonium chloride (NH_4Cl, 99.99%) were purchased from Macklin Biochemical Co., Ltd (Shanghai, China). HPLC-purified miRNA-21, miRNA-195, miRNA-21 with single mismatch, miRNA-21 with three base mismatches and carboxyl-modified molecular beacon were purchased from Sangong Biotech (Shanghai China), and validated by quality-control mass spectroscopy. The sequences is shown in table 1.

Synthesis of SiO_2 nanofibres

The flexible SiO_2 nanofibres were prepared according to a modified sol-gel approach previously reported. Briefly, a silica gel with the molar composition of H_3PO_4: TEOS: H_2O = 0.04: 1: 11 were prepared by hydrolysis and polycondensation for 12 h at room temperature. Then, an equivalent weight of 10 wt% PVA aqueous solution was added into the silica gel and stirred for another 10 h. For the electrospinning process, the silica precursor solution was transferred into a 10-mL syringe. The applied voltage and tip-to-collector distance was fixed to be 10 kV and 12 cm, respectively. The feeding rate was set at 0.5 mL h^{-1}. The as-spun nanofibres were dried at 37 ^oC overnight and calcined at 800 ^oC for 3 h to remove PVA.

Growth of $NaYF_4$:Yb,Er nanoparticles on SiO_2 nanofibres

$NaYF_4$:Yb,Er nanoparticles (UCNP) assembled SiO_2 (SiO_2@UCNP) nanofibres were prepared via a solvothermal method. Firstly, a transparent solution, labeled as solution A, was prepared by dissolving 1.2 mmol of NaCl, 0.48mmol of $YCl_3 \cdot 6H_2O$, 0.108 mmol of $YbCl_3 \cdot 6H_2O$ and 0.012 mmol of $ErCl_3 \cdot 6H_2O$ in 9 ml of ethylene glycol (EG). Then, the other transparent solution, labeled as solution B, was obtained through mixing 3.0 mmol of NH_4F and 0.006 mmol of hydrophilic polyethyleneimine (PEI) in 6 ml of EG. Subsequently, solution A was added into solution B, and stirred for 10 minutes. Afterwards, the precursor solution with SiO_2 membrane was sealed into a 25 mL Teflon-lined autoclave and kept the temperature at 200 °C for 120 minutes before cooled down to room temperature. Finally, the as-prepared SiO_2@UCNP membrane was rinsed with distilled water and ethanol several times, and dried at 80 ^oC for 12 h. To optimize the loading of UCNPs, varied solvothermal time (90, 120, 150 min) and different mass of SiO_2 nanofiber (5, 10, 15 mg) were explored.

Conjugation of Molecular beacon with UCNF (Table 1)

Molecular beacons (MB) were covalently conjugated to SiO_2@UCNP nanofibres through the amine groups of PEI on SiO_2@UCNP nanofibres and carboxyl groups of MBs. Firstly, carboxyl group-modified molecular beacon (30 µL, 100 µM), N-hydroxy-succinimide (NHS, 200 µL, 2 mg L^{-1}) and 1-ethyl-3-(3-dimethylaminopropy) carbodiimide (EDC, 400 µL, 2 mg mL^{-1}) were incubated in 2.5 mL of ultrapure water at 37 ^oC for 1 h. Then 5 mg of SiO_2@UCNP membrane was added to the above solution and reacted at 37 ^oC for 24 h. The MB grafted SiO_2 membrane were finally obtained by rinsing with ultrapure water several times and stored at 4 ^oC for further use.

Detection of target miRNA

5 mg of MB grafted SiO_2@UCNP membrane (miRNA biosensor membrane) was immersed into 2 mL of target miRNA (miRNA-21) with the concentrations ranging from 2 nM to 500 nM and incubated at 37 ^oC for 1 h. Then the miRNA biosensor membrane was rinsed with ultrapure water several times and dried at 37 ^oC for 24 h. To test the specificity of the miRNA biosensor membrane, miRNA-21 with single-base mismatch, miRNA-21 with three-base mismatch and miRNA-195 with a concentration of 10 nM were used via a similar protocol. Similar procedure was used for the detection of miRNA-21 in 10 % fetal bovine serum.

Characterization

The morphology, microstructure and composition of UCNP and fibres were investigated by a Hitachi SU-70 field-emission scanning electron microscope (FESEM) and a FEI Tecnai F20 high-resolution transmission electron microscope (HRTEM). The UCPL spectra were obtained under the excitation of a continuous laser with a wavelength of 980 nm from a fluorescence spectrophotometer (PL, FLSP920, Edinburgh). FTIR spectra were recorded on a PerkinElmer 580B (Tensor 27, Bruker) infrared spectrophotometer using the KBr pellet technique. The zeta potential of materials was measured by a Zetasizer (Zetasizer Nano-ZS, Malvern). UV-vis spectroscopy measurements were performed on a TU-1810 UV-vis spectrophotometer. A thermogravimetric/differential scanning calorimetry (TG-DSC, DSCQ1000, the USA) was used to verify the thermal decomposition of as-spun fibres. The X-ray diffraction (XRD) patterns were obtained by a thermo ARL X'TRA powder diffractometer.

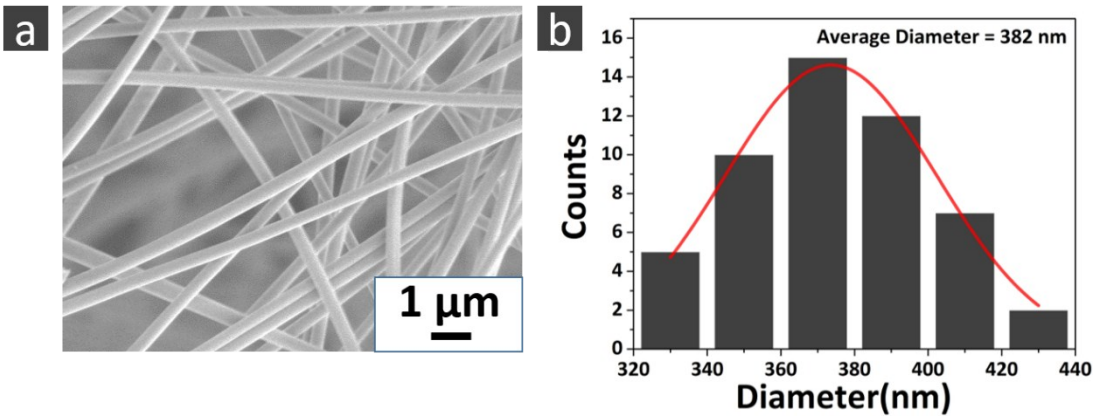

Fig. S1 (a) SEM image and (b) diameter distribution of electrospun SiO_2 fibres.

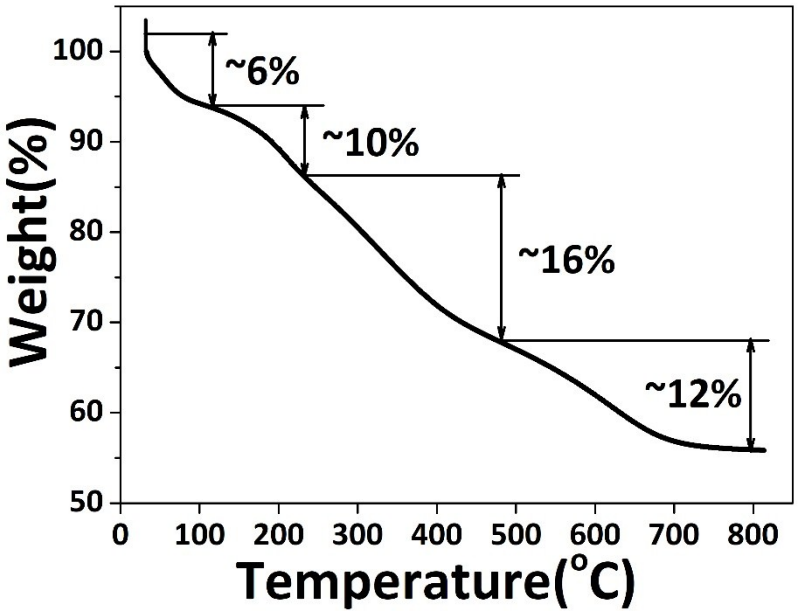

Fig. S2 TG analysis of electrospun PVA/SiO_2 fibres.

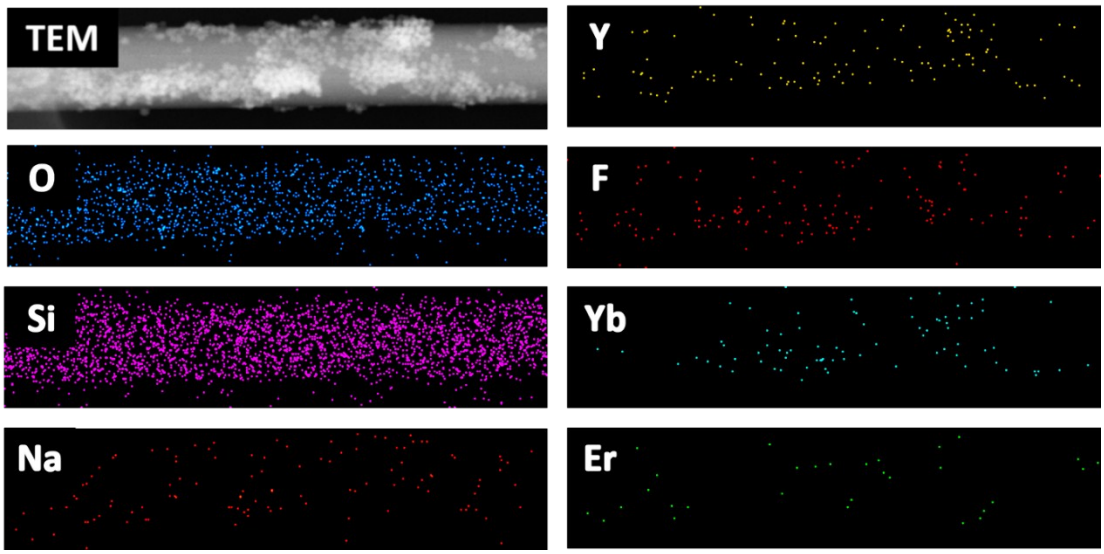

Fig. S3 Elemental mapping of SiO_2@UCNP fibres.

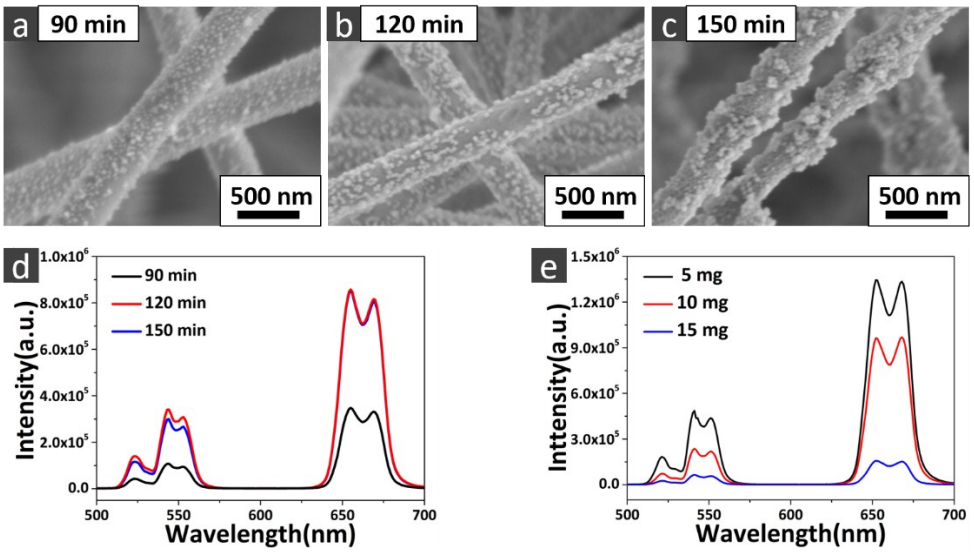

Fig.S4 (a) and (b) Upconversion luminescence spectra of electrospun SiO_2@UCNP nanofibers of varied solvothermal time and different mass of SiO_2 nanofiber added; (c)-(e) SEM images of electrospun SiO_2@UCNP nanofibers of varied solvothermal time: 90, 120, 150 min, respectively.

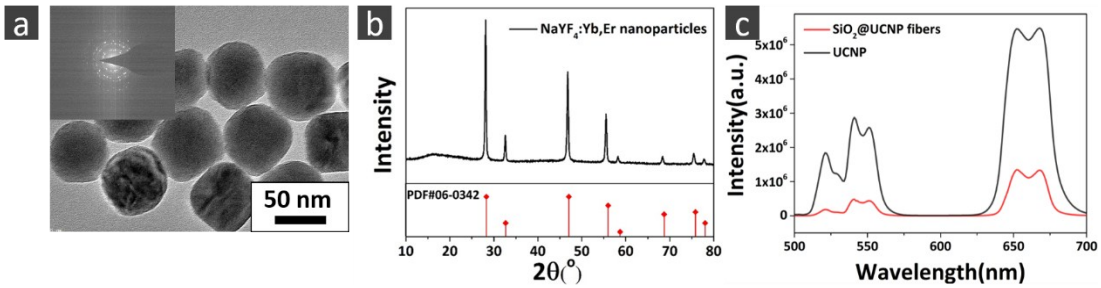

Fig. S5 (a) TEM image and (b) XRD pattern of $NaYF_4$:Yb,Er nanoparticles; (b) Upconversion luminescence spectra of SiO_2@UCNP fibres and UCNP.

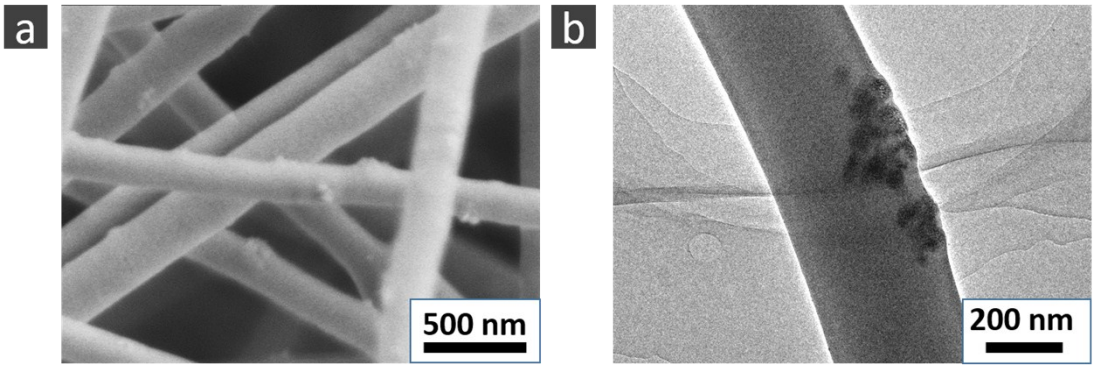

Fig. S6 SEM (a) and TEM (b) images of electrospun $NaYF_4$:Yb,Er nanoparticles embedded SiO_2 nanofibres reported previously.

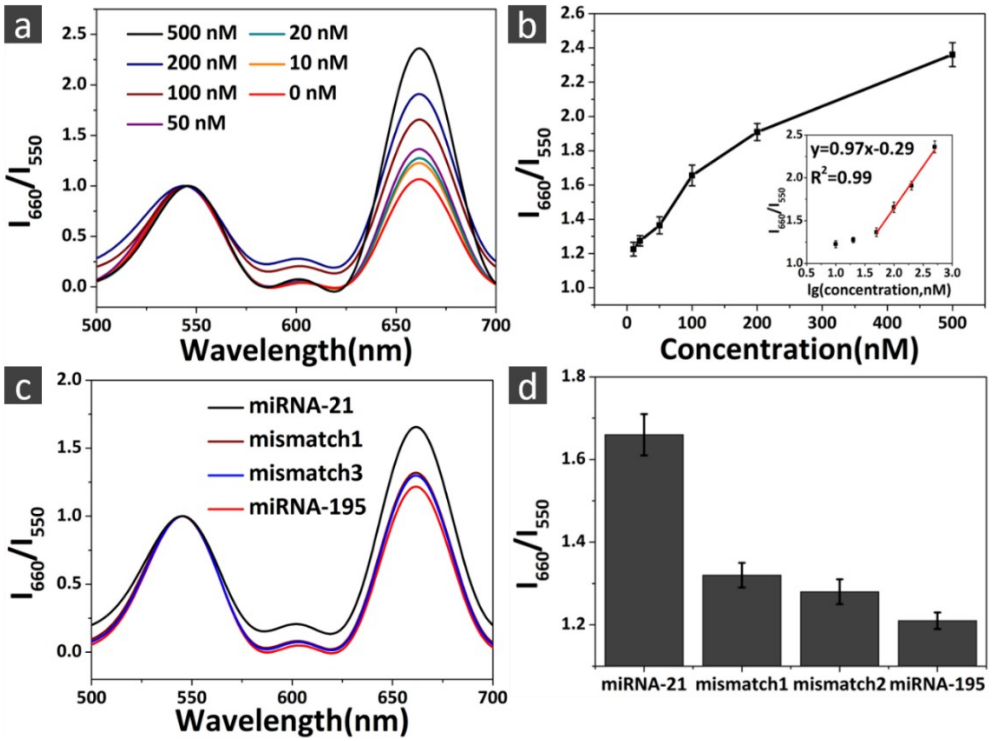

Fig.S7 (a) Upconversion luminescence spectra of SiO2@UCNP-MB biosensor incubated with 10%vol fetal bovine serum with different miRNA-21 concentrations; (b) Relationship between I660/I550 ratio and miRNA-21 concentration in fetal bovine serum; (c) and (d) specific detection of miRNA-21, miRNA-21 with single base mismatch, miRNA-21 with three bases mismatches and miRA-195 in 10% fetal bovine serum.

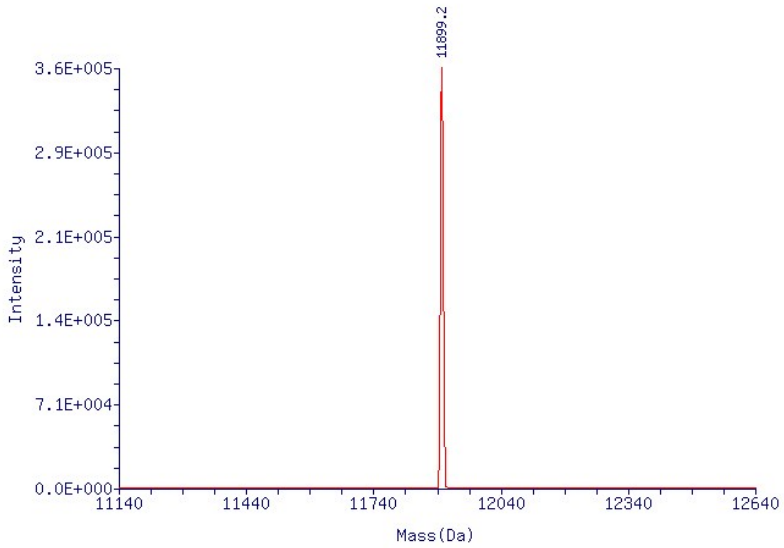

Fig. S8 Mass data of molecular beacons.