Electronic Supplementary Material (ESI) for Analytical Methods
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Supporting Information

A turn-on upconversion fluorescence resonance energy transfer biosensor for ultrasensitive endonuclease detection

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Supplementary Figures and Table

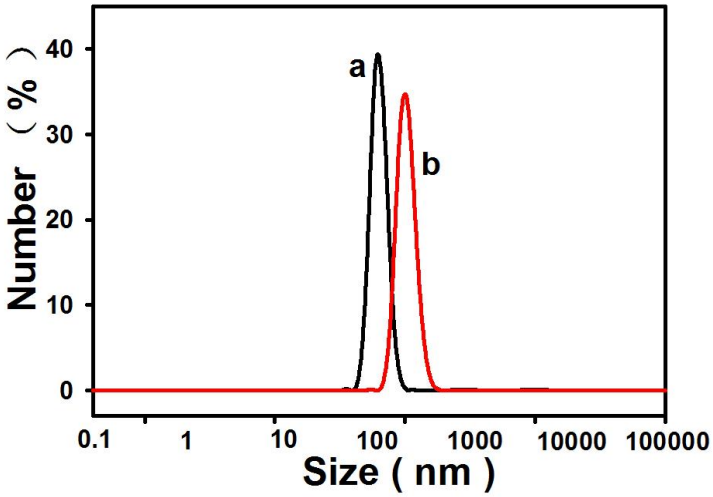

Figure. S1 The hydrodynamic size distribution of (a) the OA-coated UCNPs in cyclohexane and (b) the DNA-functionalizable UCNPs in water, determined by the dynamic light scattering. The DNA-functionalizable UCNPs were well-dispersed in water with a mean hydrodynamic diameter of about 98 nm. In comparison with the OA-coated UCNPs dispersed in cyclohexane (ca. 72 nm), the DNA-functionalizable UCNPs increase of approximately 26 nm in diameter was in agreement with the layer of the DNA stretch in the water.

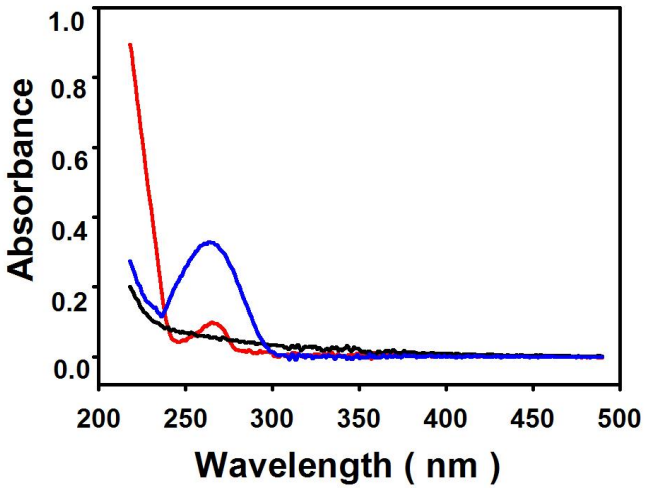

Figure. S2 The UV−vis absorption spectrum of the OA-UCNPs (black line), the DNAs (blue line) and the DNA-UCNPs (red line). A ultraviolet absorption maximum of the DNAs at approximately 260 nm, there no absorption peaks appeared in the UV−vis spectrum of the OA-UCNPs, and a new absorption peak at approximately 260 nm was observed in the spectrum of the DNA-UCNPs as a result of the amount of DNAs combined with UCNPs.

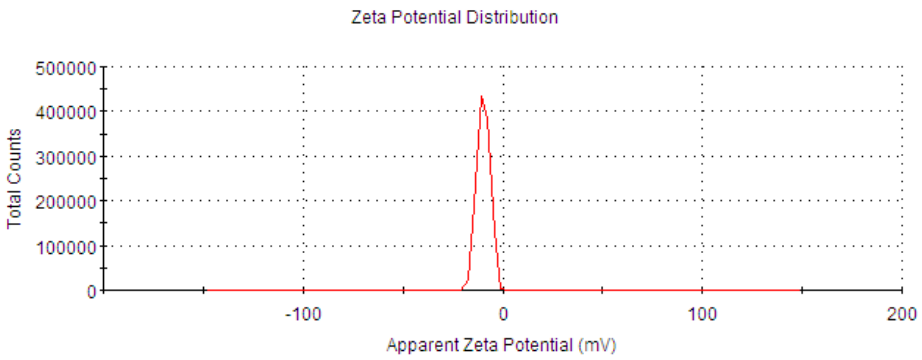

Figure. S3 Zeta potential experiments of the as-prepared DNA-functionalizable $NaYF_4$:Yb,Tm@$NaYF_4$ UCNPs. The zeta potential of the resulting DNA- modified UCNPs was -9.6 mV.

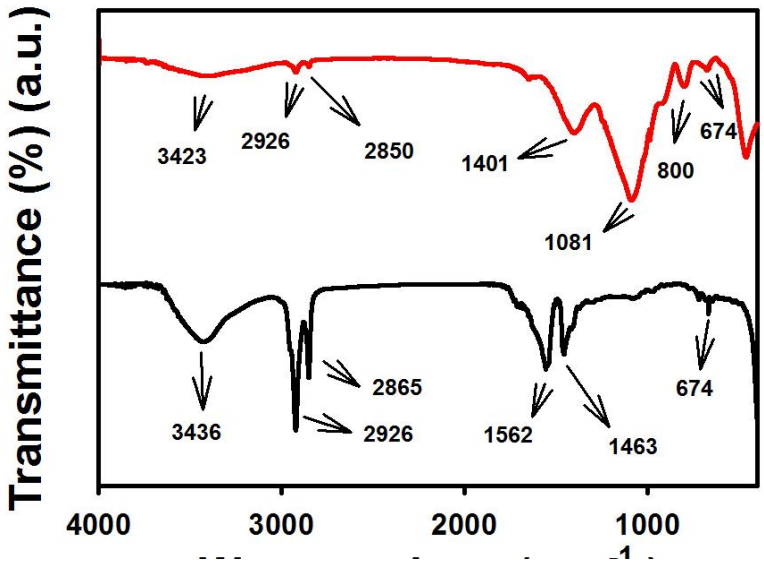

Figure. S4 FT-IR spectra of the as-prepared OA-coated UCNPs (black carve) and DNA-functionalizable UCNPs (red carve). A prominent transmission bands at 1400 and 1082 cm^{-1} for the DNA-functionalizable UCNPs, which were not observed for the UCNPs coated with oleic acid. These bands were ascribed to the stretching vibrations of the glycosidic bond and the stretching vibrations of phosphate diester bond in DNA. Two strong bands centered at 1562 and 1463 cm^{-1} were observed in the OA-coated UCNPs spectrum, these bands were assigned to the asymmetric and symmetric stretching vibrations of the carboxylate anions on the surface of the UCNPs. The absorption bands around 2926 and 2849 cm^{-1} were slightly decreased in the DNA-functionalizable UCNPs as compared to those coated with oleic acid, attributed to the decreased amount of the methylene (–CH2–) in the DNA coating.The UCNPs, either coated with oleic acid or DNA, exhibited a broad band around ~3436 cm^{-1}, corresponding to the asymmetric and symmetric stretching vibrations of the hydroxy (–OH).

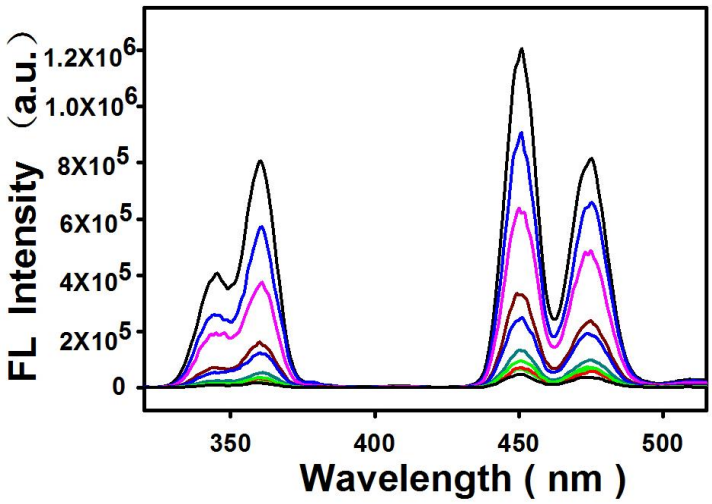

Figure. S5 Fluorescence spectra of DNA-UCNPs after incubation with various concentrations of GO.

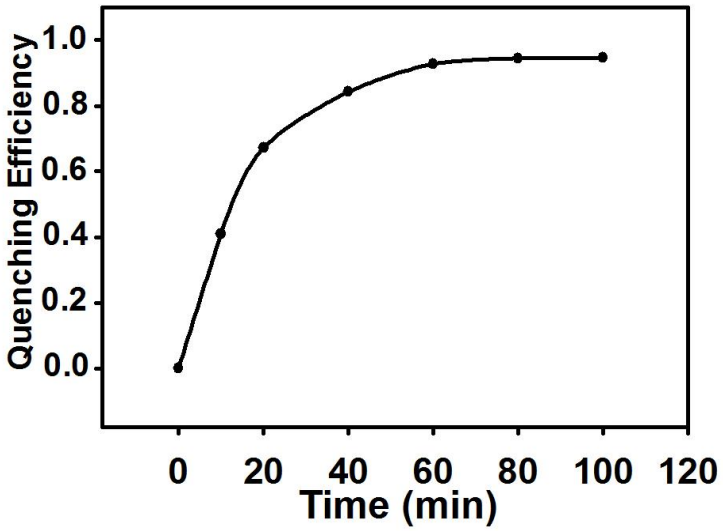

Figure. S6 Effect of the incubation time of the DNA-UCNPs with GO on the upconversion fluorescence quenching. The fluorescence intensity decreased rapidly with the increase in the reaction time before 60 min, and then reached a fixed value after 60 min. The concentrations of DNA-UCNPs and GO were 50 μg mL^{-1} and 80 μg mL^{-1}, respectively.

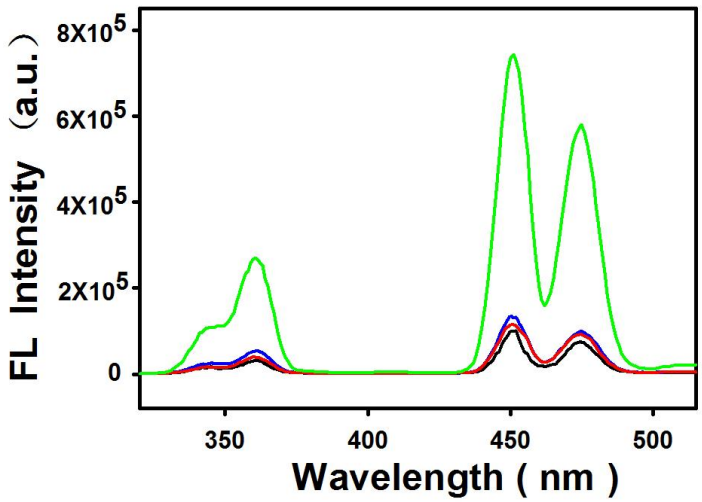

Figure. S7 Upconversion fluorescence spectra of DNA-modified UCNPs + GO (black curve), DNA-modified UCNPs + thrombin + GO (red curve), DNA-modified UCNPs + Exonuclease III + GO (blue curve) and DNA-modified UCNPs + S1 nuclease + GO (green urve). The concentrations of thrombin, Exonuclease III and S1 nuclease were both 5×10^{-2} units mL^{-1}, the concentrations of DNA-UCNPs and GO were 50 μg mL^{-1} and 80 μg mL^{-1}, respectively.

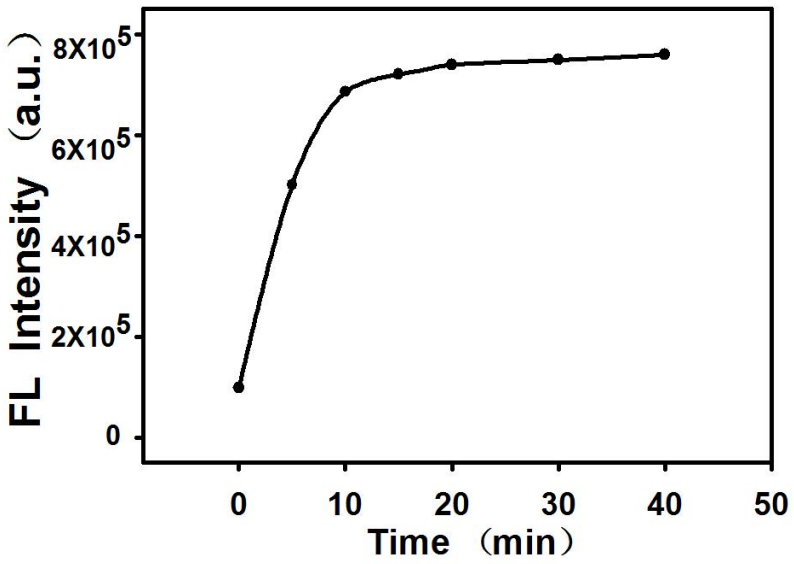

Figure. S8 Effect of the incubation time of the DNA-UCNPs with S1 nuclease on the upconversion fluorescence spectra. The fluorescence intensity increased rapidly with the increase in the reaction time before 10 min, and then reached a fixed value after 10 min. The concentrations of S1 nuclease was 5×10^{-2} units mL^{-1}, the concentrations of DNA-UCNPs and GO were 50 μg mL^{-1} and 80 μg mL^{-1}, respectively.

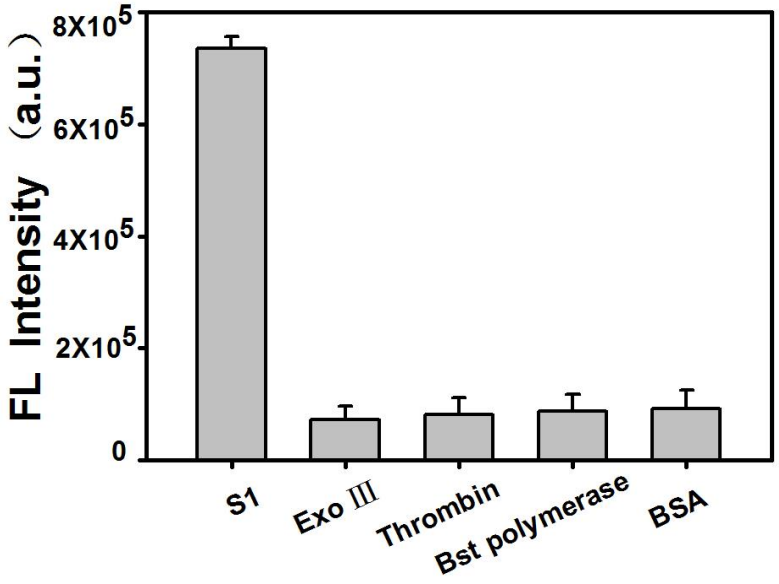

Figure. S9 Selectivity of the assay system for nuclease S1. Nuclease S1 and Exonuclease III were at a concentration of 3×10^{-2} units mL^{-1}. Bst polymerase and Thrombin were at a concentration of 0.5 units mL^{-1}. BSA was at a concentration of 0.1 mg mL^{-1}. Error bars represented standard deviations from three repeated experiments.

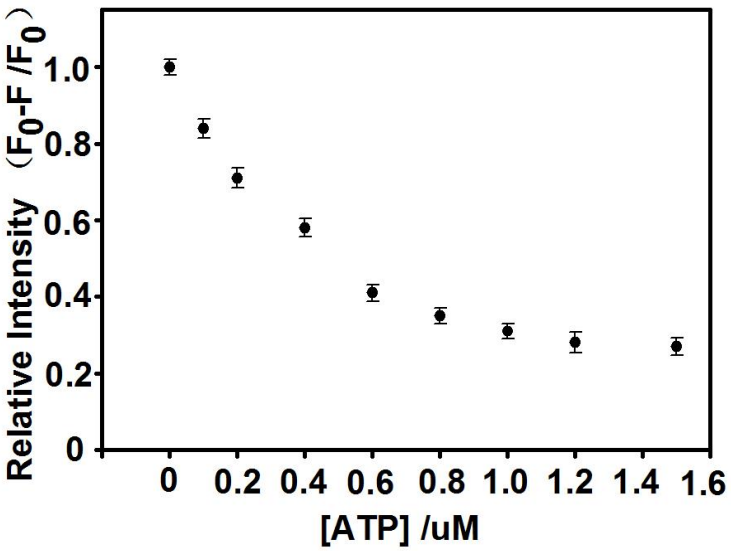

Figure. S10 The Inhibitory effect of ATP on the activity of S1 nuclease. The concentration of S1 nuclease was 5×10^{-2} units mL^{-1}, the concentrations of DNA-UCNPs and GO were 50 μg mL^{-1} and 80 μg mL^{-1}, respectively. Error bars represented standard deviations from three repeated experiments.

Table S1 The comparison of sensors for the determination of S1 nuclease.

Method	Tool	LODa (units mL^{-1})	Ref
Colorimetric	positively charged gold nanoparticles	4.3	S1
Fluorescence	cationic conjugated polymer and fluorescein-labeled DNA probe	2.8×10^{-2}	S2
Fluorescence	fluorophore and quencher-labeled molecular beacon	3	S3
Fluorescence	conjugated polymer and DNA/intercalating dye complex	2.6×10^{-2}	S4
Fluorescence	aggregation-induced emission (AIE) of silole	7.5	S5
Fluorescence	G-quadruplex and protoporphyrin IX	4.0×10^{-2}	S6
Fluorescence	double-stranded DNA-templated copper nanoparticles	0.3	S7
Fluorescence	C-rich DNA-templated silver nanoclusters	1	S8
Fluorescence	poly T-templated fluorescent CuNPs	5.0×10^{-4}	S9
Fluorescence	guanine-rich DNA sequences and DNA–silvernanoclusters	1.0×10^{-2}	S10
Fluorescence	DNA-functionalizable UCNPs - graphene oxide FRET nanosystem	1.0×10^{-4}	This work

3. References

S1 R. Cao, B. Li, Y. Zhang and Z. Zhang, *Chem. Commun.*, 2011, **47**, 12301−12303.

S2 F. Feng, Y. Tang, F. He, M. Yu, X. Duan, S. Wang, Y. Li and D. Zhu, *Adv. Mater.*, 2007, **19**, 3490−3495.

S3 J. J. Li, R. Geyer and W. Tan, *Nucleic Acids Res*,. 2000, 28, e52.

S4 F. Pu, D. Hu, J. Ren, S. Wang and X. Qu, *Langmuir.*, 2010, **26**, 4540−4545.

S5 M. Wang, D. Zhang, G. Zhang, Y. Tang, S. Wang and D. Zhu, *Anal. Chem.*, 2008, **80**, 6443−6448.

S6 Z. Zhou, J. Zhu, L. Zhang, Y. Du, S. Dong and E. Wang, *Anal. Chem*., 2013, **85**, 2431−2435.

S7 R. Hu, Y. R. Liu, R. M. Kong, M. J. Donovan, X. B. Zhang, W. Tan, G. L. Shen and R. Q. Yu, *Biosens. Bioelectron.*, 2013, **42**, 31−35.

S8 Y. Xiao, F. Shu, K. Y. Wong and Z. Liu, *Anal. Chem.*, 2013, **85**, 8493−8497.

S9 Z. H. Qing, X. X. He, T. P. Qing, K. M. Wang, H. Shi, D. G. He, Z. Zou, L. Yan, F. Z. Xu, X.S. Ye and Z.G. Mao. *Anal. Chem*. 2013, **85**, 12138−12143**.**

S10 X. Tian, X. J. Kong, Z. M. Zhu, T. T. Chen and X. Chu., *Talanta*., 2015, **131**, 116–120