Supporting Information

Cobalt Oxyhydroxide Assembled Upconversion Nanoparticles as a Ratiometric Nanoprobe for Ascorbic Acid Detecting and Imaging

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Materials and instruments

Yb_2O_3 (99.9%), Tm_2O_3 (99.9%), Y_2O_3 (99.9%), Gd_2O_3 (99.9%), were obtained from Tianjin Guangfu Fine Chemical Research Institute. 1-octadecene (90%), oleic acid (90%), and $YCl_3·6H_2O$ were purchased from Alfa Aesar. The other reagents used without further purification were received from commercial sources. Thermo gravimetric analysis (TGA) was conducted on Netzsch STA449F3 Jupiter® thermal analyzer up to 800 °C at a heating rate of 10 $°C·min^{-1}$ in N_2 atmosphere. Transmission electron microscopy (TEM) was obtained on a Tecnai-G2-F30 (300 kV). X-ray diffraction (XRD) pattern of the synthesized products were recorded with a Rigaku D/MAX 2400 X-ray diffractometer using Cu Kα radiation (λ = 0.154056 Å). Fluorescence spectra were recorded on a Hitachi F-7000 spectrofluorometer equipped with a 0-5 W adjustable CW laser (980 nm, Connect Fiber Optics, China) as the excitation source. The lifetimes were determined by FLS920 of Edinburgh Instruments. Cyclic voltammograms were identified by a CHI660B electrochemical Workstation (CH Instruments, Inc., USA) using platinum (Pt) wire and Ag/AgCl (*aq.* saturated KCl) as the counter and reference electrodes, respectively. Glassy carbon electrode (3 mm) was used as the working electrode with scan rate of 5 mV s^{-1}. All pH measurements were executed with a pH-10C digital pH meter. HeLa cells were provided by the Institute of Biochemistry and Cell Biology (China) were cultured for 48 h in culture in DMEM (Dulbecco's Modified Eagle's Medium, High Glucose) with 10% fetal bovine serum (FBS) in an atmosphere of 5% CO_2 and 95% at 37 ^oC with a humidified incubator.

Supporting Figures:

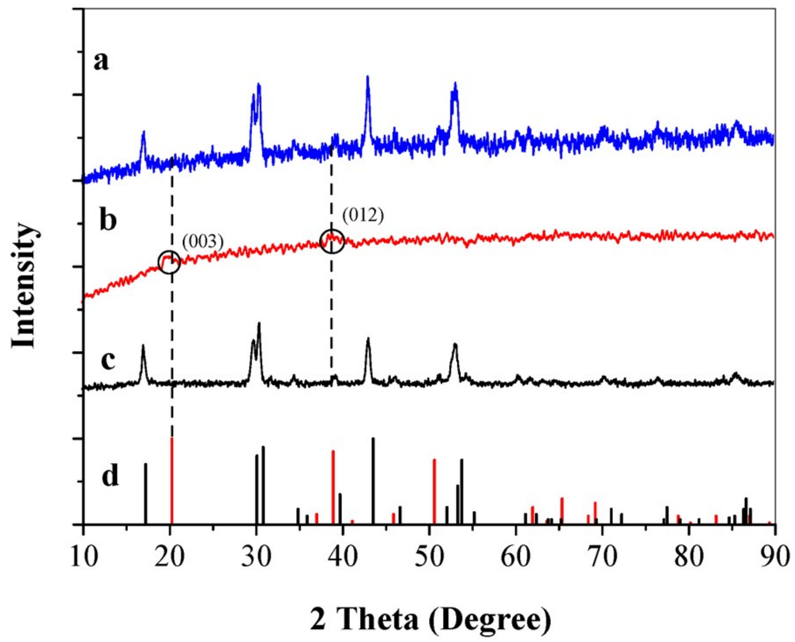

Fig. S1. XRD patterns of ligand-free core-shell UCNPs (a), CoOOH (b), and CoOOH-modified UCNPs (c), standard XRD patterns for CoOOH nanocrystals (JCPDS, Card No.07-0169) (red) and $NaYF_4$ UCNPs (JCPDS, Card No.16-0334) (black) (d).

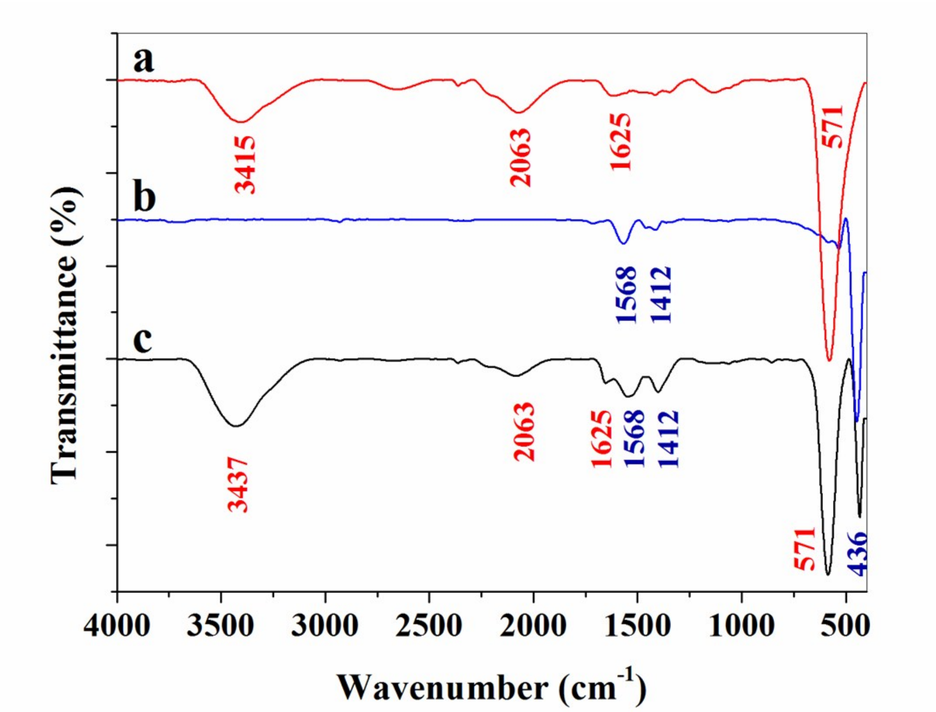

Fig. S2. FT-IR spectra of CoOOH (a), ligand-free core-shell UCNPs (b), and CoOOH modified UCNPs (c).

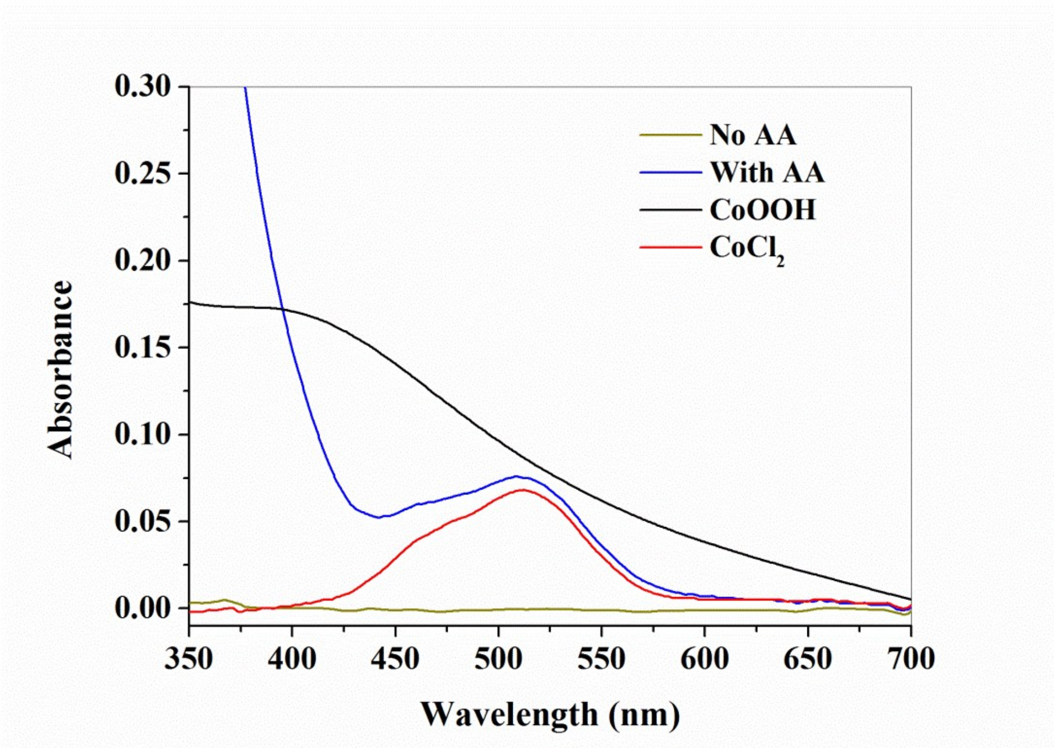

Fig. S3. UV-vis absorption of aqueous solution of $CoCl_2$ (red line), CoOOH solution (black line), supernates of CoOOH-modified UCNPs solution (brown line) and CoOOH-modified UCNPs solution with AA (blue line).

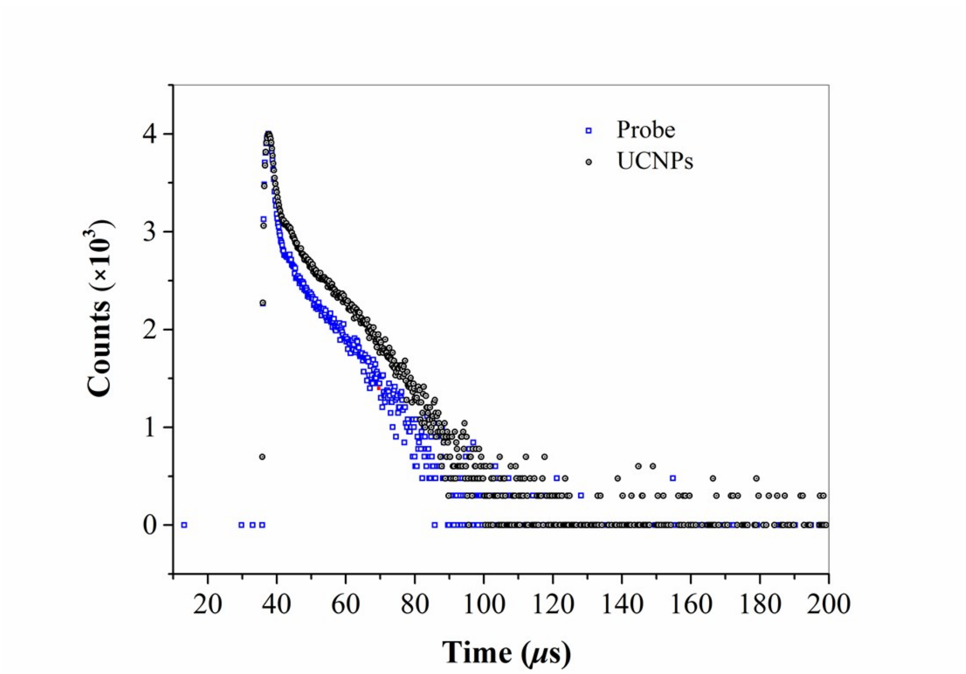

Fig. S4. The luminescence (475 nm) lifetime decay profile of bared UCNPs (black dots) and CoOOH-modified UCNPs (blue dots).

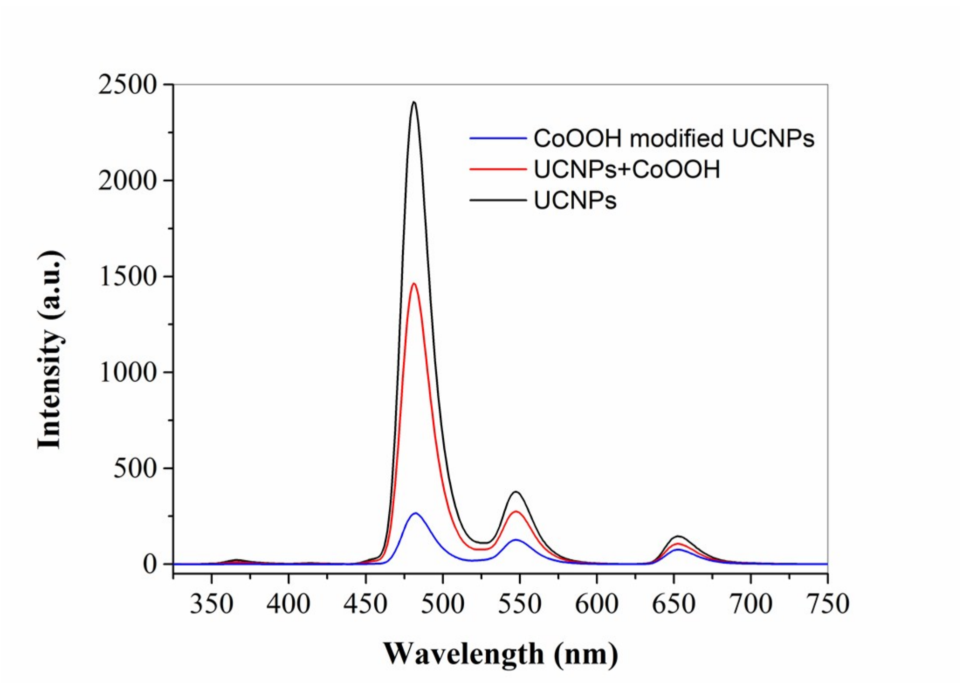

Fig. S5. UCL spectra of aqueous solutions of UCNPs (1mg/mL, black line), physical mixture of CoOOH (2 mmol) and UCNPs (blue line), and CoOOH-modified UCNPs (prepared with 2.0 mmol $CoCl_2$, red line).

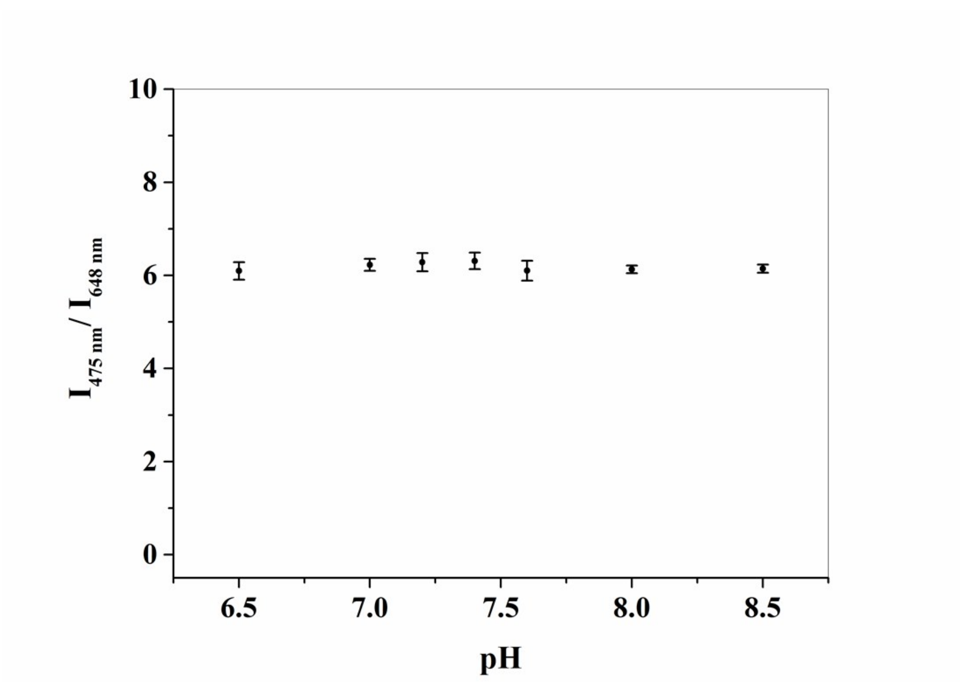

Fig. S6. UCL intensity of CoOOH modified UCNPs (1mg/mL) in different pH solutions in the absence (black dots) and presence (red dots) of AA (100 μM).

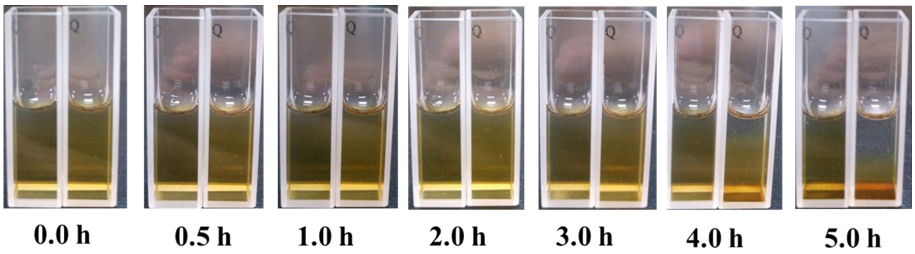

Fig. S7. Photograph changes of CoOOH-modified UCNPs (1 mg/mL) solution with (left) and without (right) 10% ethylene glycol (EG) over time. EG was also introduced as the dispersant into sensing system to improve the stability of a probe. Due to the small size of CoOOH-modified UCNPs, the improvement in our probe is limited. In this regard, EG has not been introduced in the sensing study of CoOOH-modified UCNPs nano-syestem.

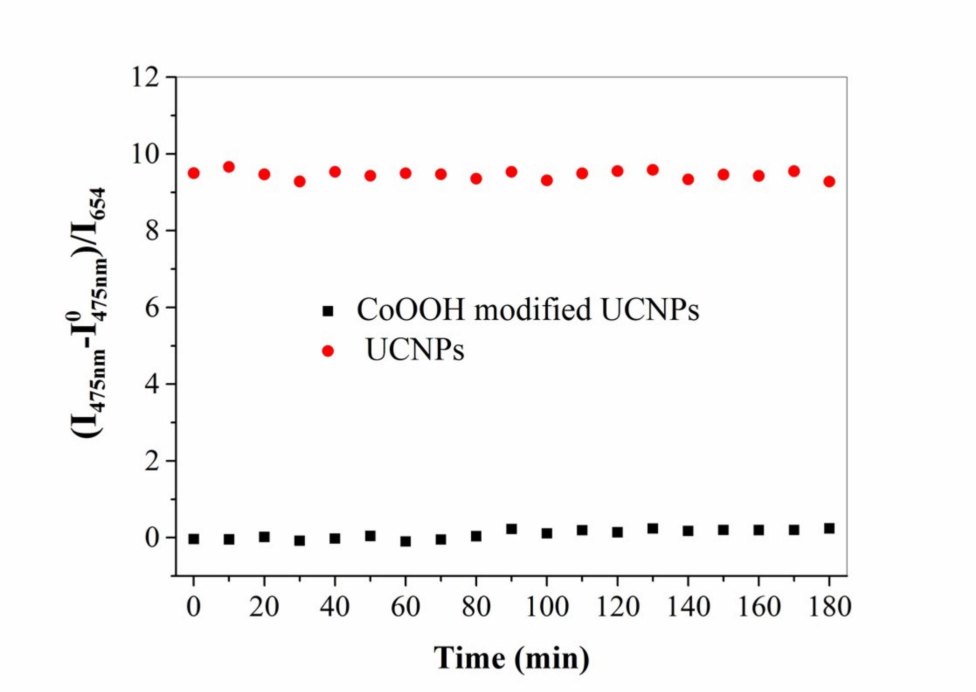

Fig. S8. Time-dependent UCL intensity ratio changes of CoOOH-modified UCNPs (1 mg/mL) (black dots) and UCNPs (red dots) depending on time in HEPES (10 mM, pH = 7.4).

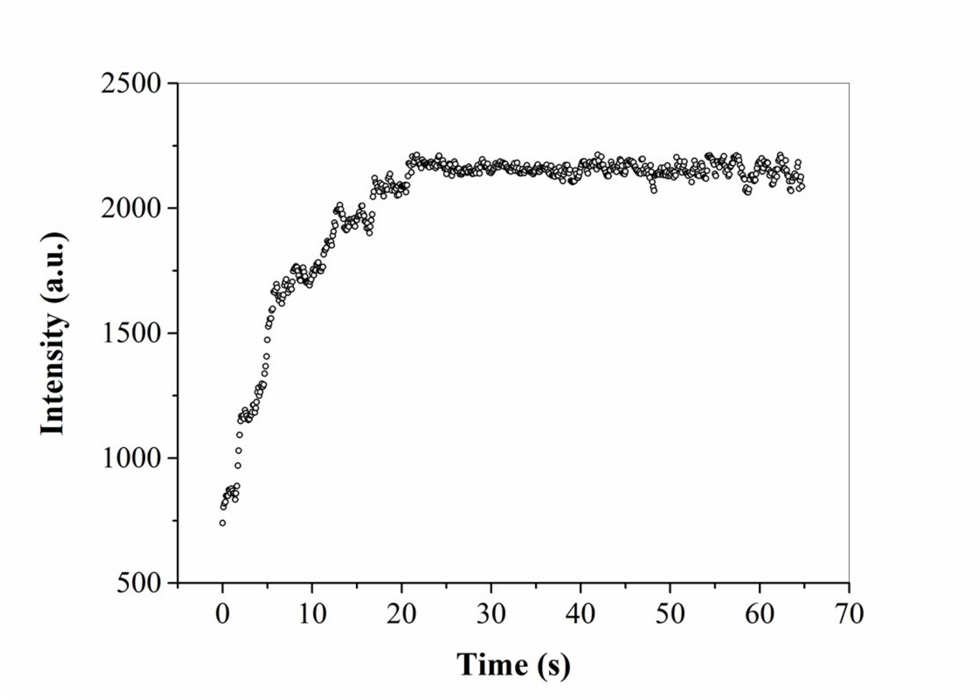

Fig. S9. Time-dependent UCL intensity (475 nm) changes of CoOOH-modified UCNPs (1 mg/mL) with AA (100 μM)) in HEPES solution (10 mM, pH = 7.4).

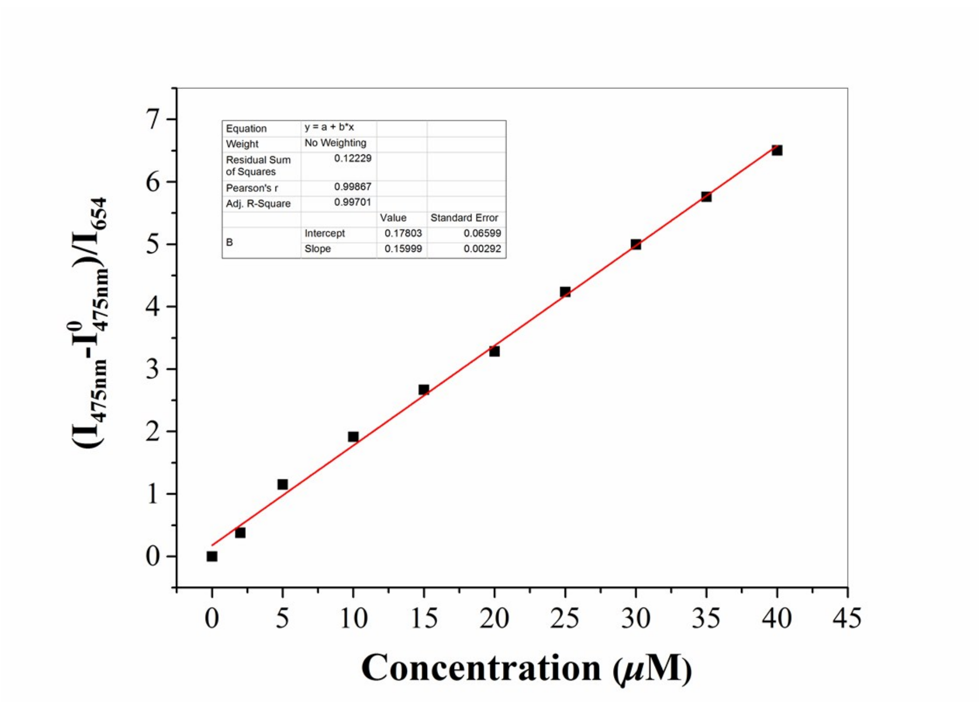

Fig. S10. UCL intensity ratio I_{475}/I_{468} changes of CoOOH modified UCNPs as a function of AA concentration in HEPES (10 mM, pH = 7.4).

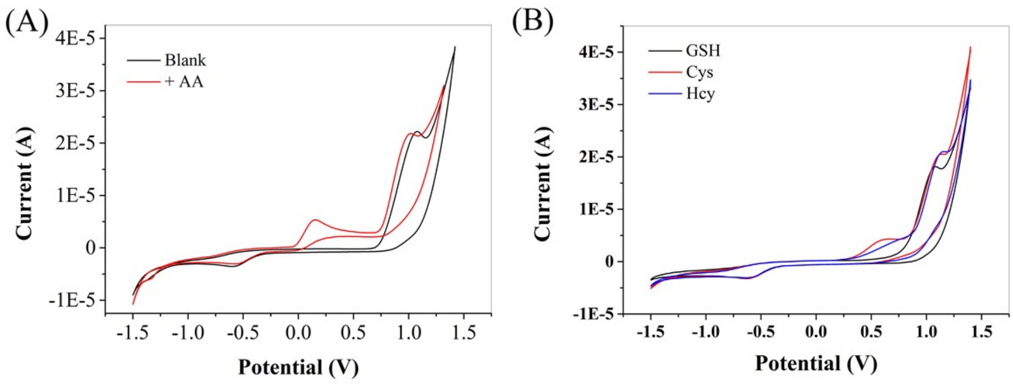

Fig. S11. Cyclic voltammograms of 1mM AA, GSH, Cys and Hcy in HEPES solution (10 mM, pH = 7.4).

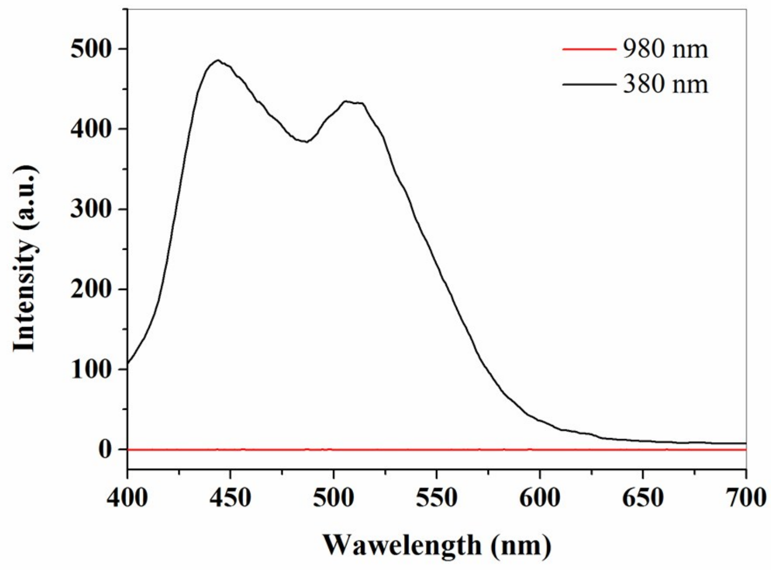

Fig. S12. UCL spectra of diluted (25 %) fetal bovine serum in the absence AA under excitation at 380 nm (blank) and 980 nm (red).

EDX

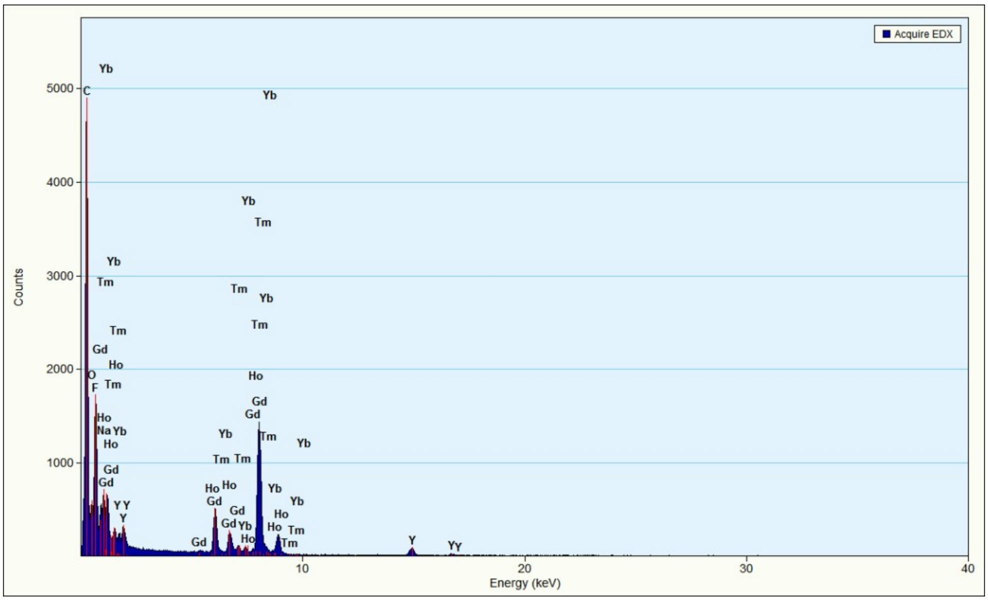

Fig. S13. EDX spectrum of UCNPs.

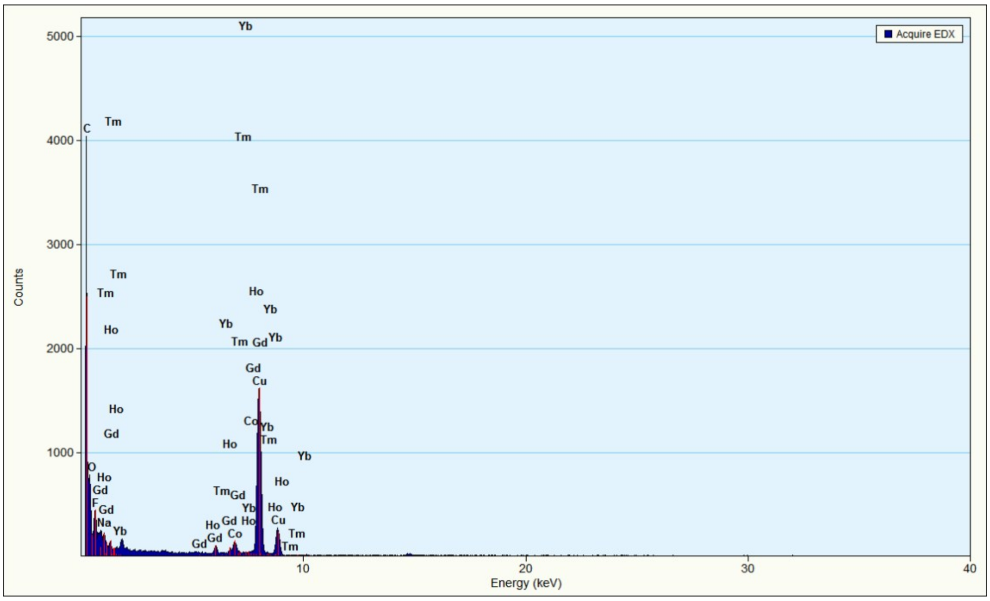

Fig. S14. EDX spectrum of CoOOH modified UCNPs.

TG-DSC:

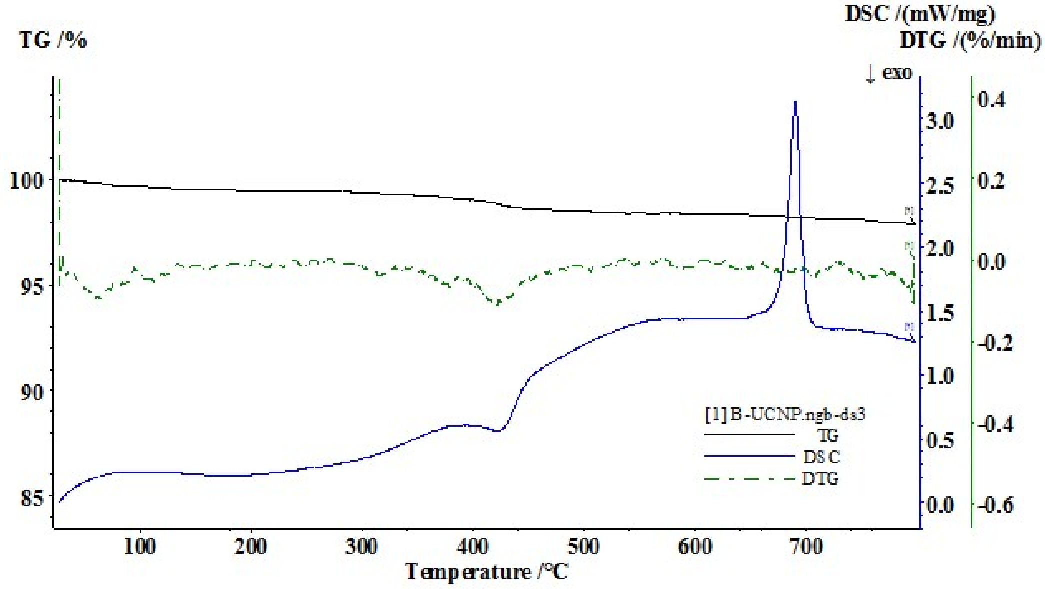

Fig. S15. TG-DSC result of ligand-free core-shell UCNPs.

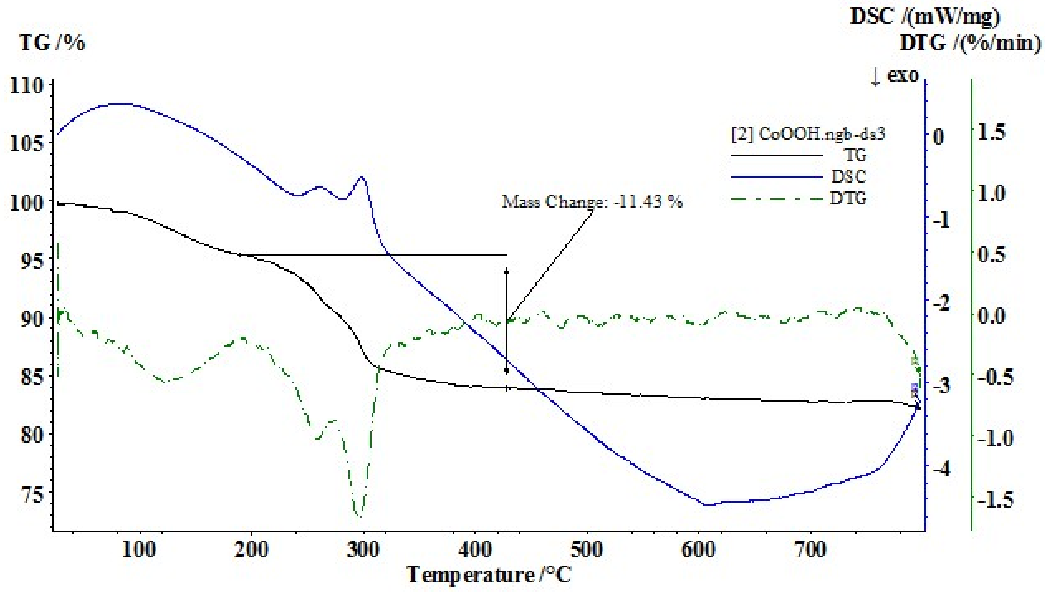

Fig. S16. TG-DSC result of CoOOH.

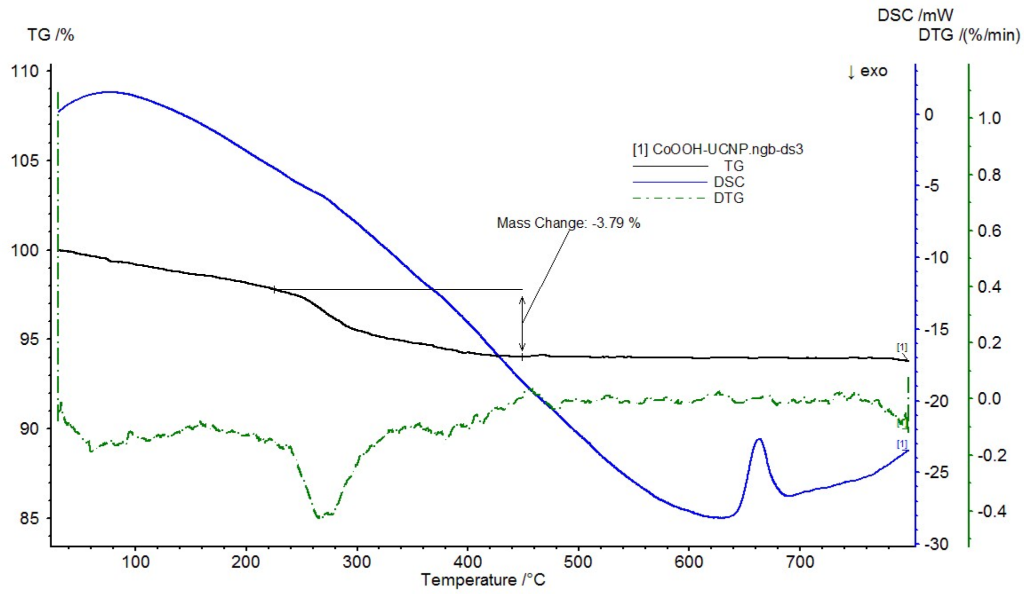

Fig. S17. TG-DSC result of CoOOH modified UCNPs.