Electronic Supplementary Information

Cobalt oxyhydroxide-modified upconversion nanosystem for sensitive fluorescence sensing of ascorbic acid in human plasma

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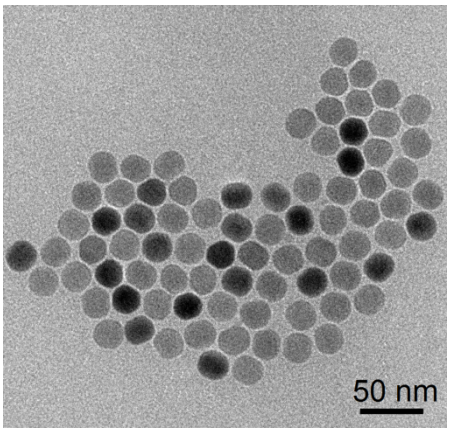

Fig. S1. TEM image of OA-coated $NaYF_4$: 30%Yb/0.5%Tm core nanoparticles.

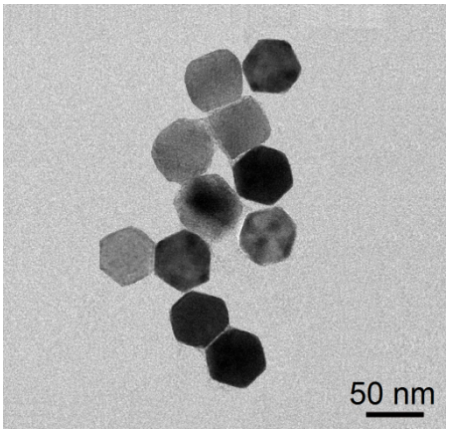

Fig. S2. TEM image of azelaic acid-coated hydrophilic $NaYF_4$:Yb/Tm@$NaYF_4$ core-shell nanoparticles.

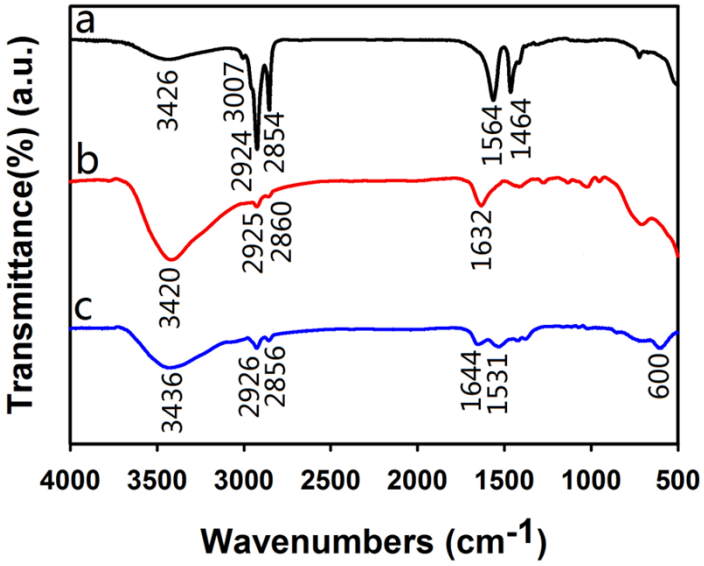

Fig. S3. FT-IR spectra of the (a) OA-coated $NaYF_4$:Yb/Tm@$NaYF_4$ nanoparticles, (b) azelaic acid-coated hydrophilic $NaYF_4$:Yb/Tm@$NaYF_4$ nanoparticles, and (c) CoOOH-modified $NaYF_4$:Yb/Tm@$NaYF_4$ nanoparticles. All of the OA-coated, azelaic acid-coated, and CoOOH-modified $NaYF_4$:Yb/Tm@$NaYF_4$ nanoparticles exhibit a broad band at around 3450 cm^{-1}, corresponding to O-H stretching vibration. A peak at 3007 cm^{-1} attributed to the =C-H stretching vibration can clearly be seen in the spectrum of the OA-coated $NaYF_4$:Yb/Tm@$NaYF_4$ nanoparticles (Fig. S3a), but this peak is apparently lost in the spectrum of azelaic acid-coated $NaYF_4$:Yb/Tm@$NaYF_4$ nanoparticles (Fig. S3b), suggesting cleavage of the -HC=CH- group. In addition, the absorption band around 1564 cm^{-1} and 1448 cm^{-1} for the OA-coated $NaYF_4$:Yb/Tm@$NaYF_4$ nanoparticles, attributed to the stretching vibration of carboxyl group in OA, was shifted to 1632 cm^{-1} for the azelaic acid-coated $NaYF_4$:Yb/Tm@$NaYF_4$ nanoparticles. The peak at 1644 cm^{-1} in Fig. S3c is the characteristic of the Co-O double bond in the crystal structure of CoOOH, while peaks at 600 cm^{-1} correspond to Co-O^{2-} complex in the assemblies.

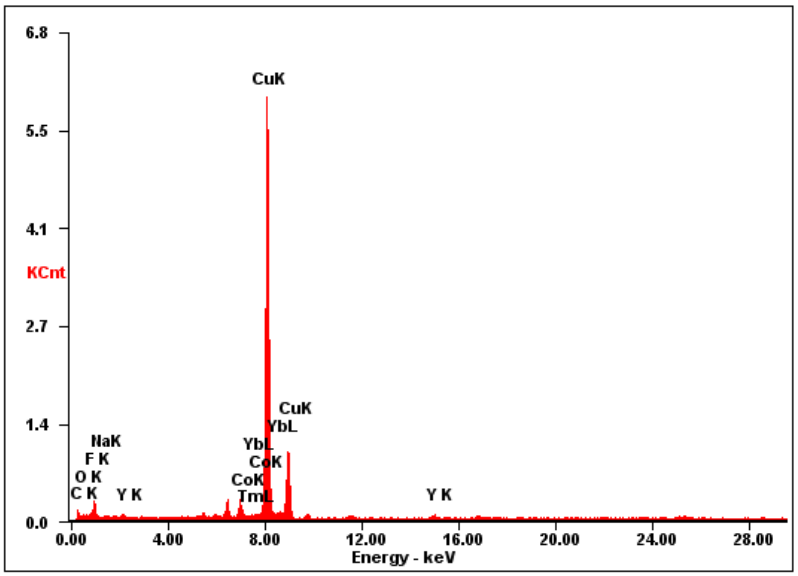

Fig. S4. Energy dispersive X-ray spectroscope (EDS) spectrum of CoOOH-modified UCNPs, indicating the presence of elemental Na, Y, F, Yb, Tm, Co, and O. Note that the strong signal of Cu comes from the copper TEM grid.

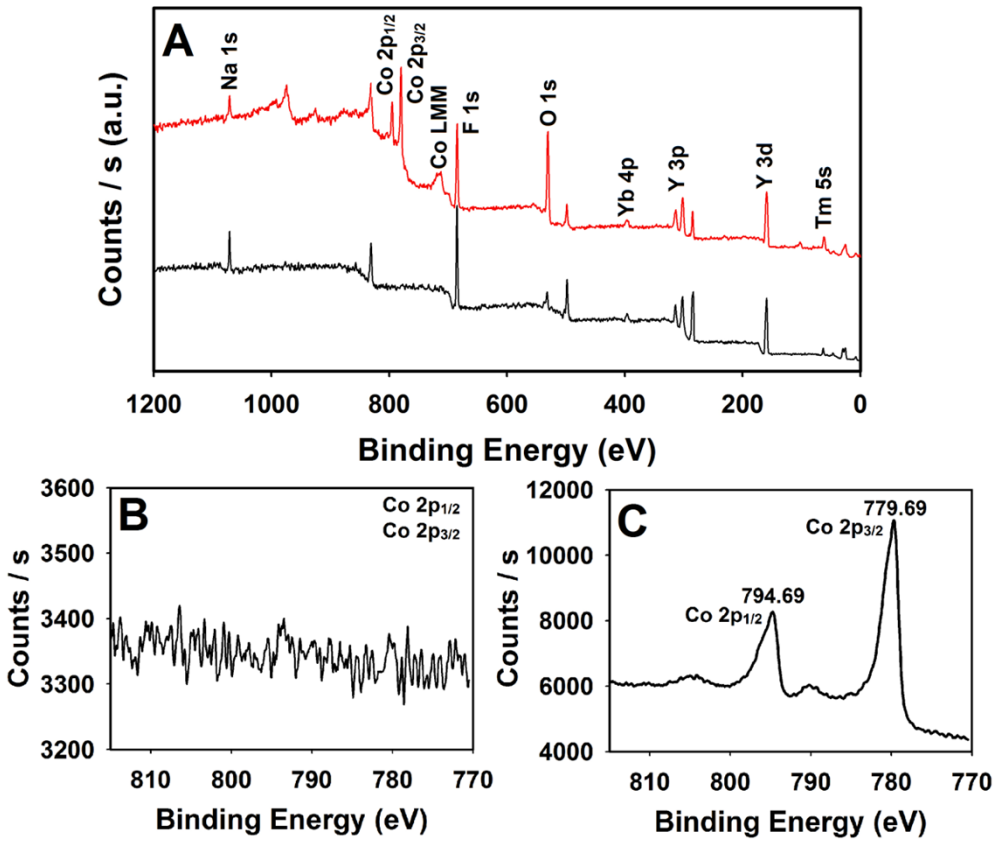

Fig. S5. (A) XPS spectra of OA-UCNPs (black line) and CoOOH-modified UCNPs (red line). (B) High resolution Co ($2p_{1/2}$) and Co ($2p_{3/2}$) XPS spectrum of the OA-UCNPs. (C) High resolution Co ($2p_{1/2}$) and Co ($2p_{3/2}$) XPS spectrum of CoOOH-modified UCNPs.

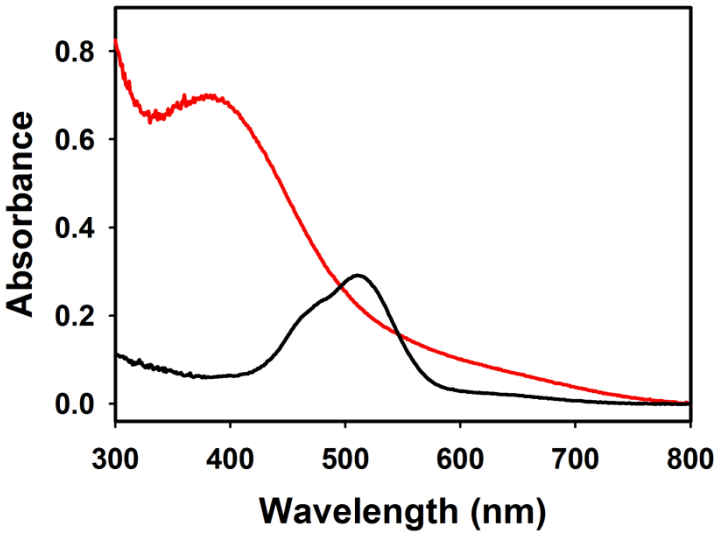

Fig. S6. Absorbance spectra of aqueous solutions of CoOOH nanoflakes (red line) and $CoCl_2$ (black line).

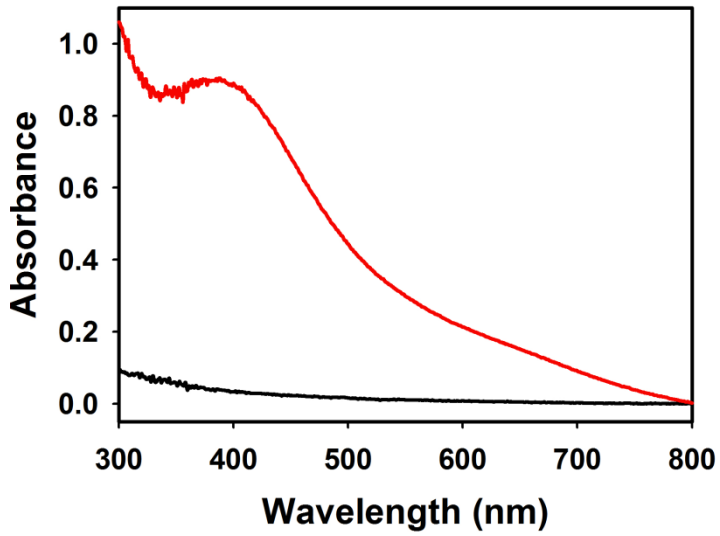

Fig. S7. Absorbance spectra of aqueous solutions of oxidized UCNPs (black line) and CoOOH-modified UCNPs (red line).

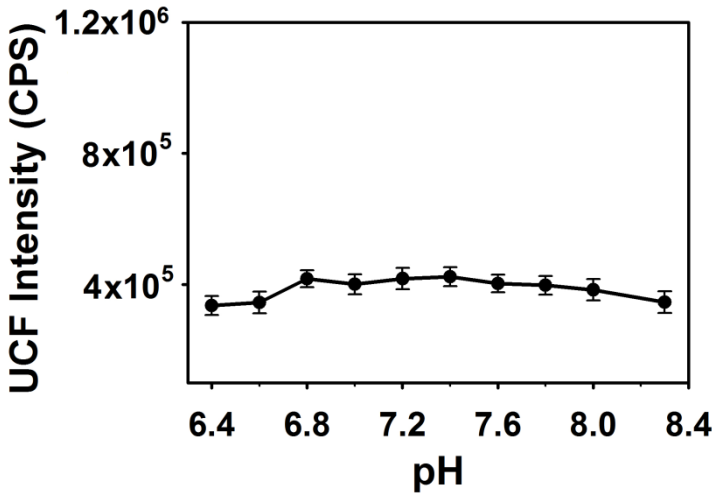

Fig. S8. Upconversion fluorescence intensity of CoOOH-modified UCNPs (0.5 mg/mL) in 10 mM PB buffer with different pH.

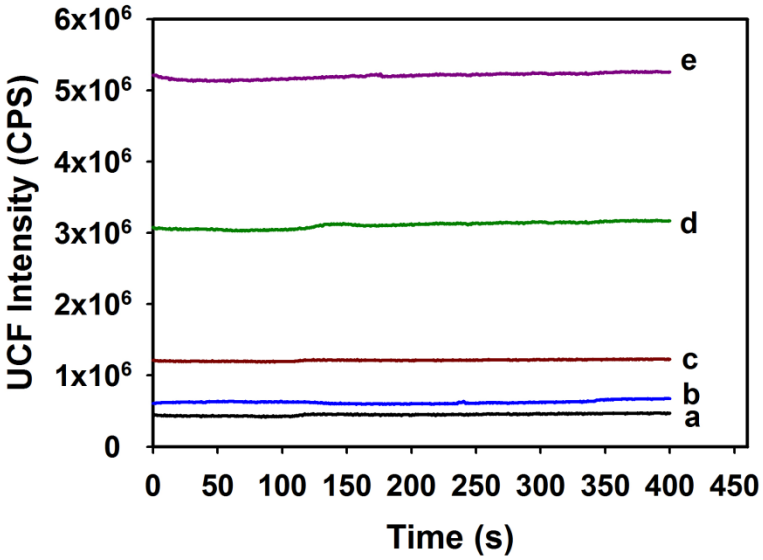

Fig. S9. Time-dependent fluorescence recovery curves of CoOOH-modified UCNPs at 360 nm obtained for AA of 0 (black line), 2 (blue line), 10 (red line), 40 (green line), and 120 μM (purple line).

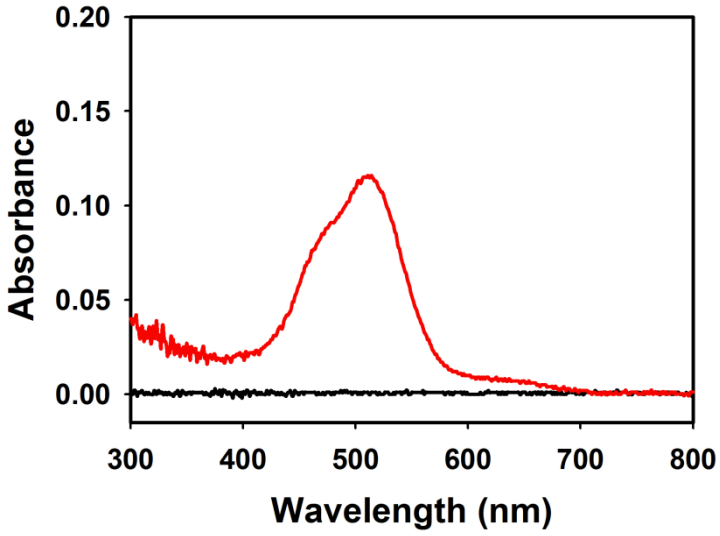

Fig. S10. Absorbance spectra of the supernates of CoOOH-modified UCNPs solution (black line) and CoOOH-modified UCNPs solution with AA (red line).

Table S1 Analytical results of AA in human plasma sample using the upconversion FRET-based nanosystem.

sample	measured (μM)	added (μM)	found (μM)	recovery (%)	RSD (n=3)
human plsama	6.8	5.0	11.3	96	5.2%
		15.0	22.6	104	6.1%
		25.0	32.2	101	4.5%