Supporting information

Blue emission-dominated $NaYbF_4$@$NaYF_4$:2%Ho@$NaYF_4$ upconversion nanoparticles for detecting ascorbic acid

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1. EXPERIMENTAL SECTION

1.1 Materials.

Ytterbium oxide (Yb_2O_3, 99.9%), yttrium oxide (Y_2O_3, 99.99%), holmium oxide (Ho_2O_3, 99.99%), sodium oleate (NaOA, 98%), sodium trifluoroacetate (Na-TFA, 97%),1-octadecene (ODE, > 90%), tetrafluoroborateanion ($NOBF_4$, 0.95), polyacrylic acid acrylic acid polymer (PAA, Solid content, 40%, M.W~2000), 2-(4-Morpholino) ethanesulfonic acid (MSE, 0.2 M, pH=6), glucose (Glu, 98%) were purchased from Shanghai Maclin Biochemical Technology Co., LTD. Oleic acid (OA, AR), $NaNO_3$(> 97%), $NaNO_2$(> 98.5%) were purchased from Shanghai Aladdin Biochemical Technology Co., LTD. N,N-Dimethylformamide (DMF, 99.5%), n-hexane(AR), ascorbic acid (AA, 99.8%), KCl (99.5%), sucrose (SUC, AR), glycine (Gly, 99%), glutathione (GSH, 99%) were purchased from Chengdu Kelong Chemical Co. LTD. Citric acid (CA, 99.5%), alanine (Ala, 99%), cysteine (Cys,99%) were purchased from Adamas Pharmaceuticals, Inc. N-Ethylmaleimide (NEM, 98%) was purchased from Sa'en Chemical Technology (Shanghai) Co., Ltd. Ethanol was purchased from Chengdu Jinshan Chemical Reagent Co. LTD. All chemicals were used as received without any further purification.

$LnCl_3$ (Ln = Y, Yb, Ho) was prepared by dissolving the corresponding metal oxides in water containing an appropriate amount of hydrochloric acid solution, and then evaporating the water completely.

1.2 General characterizations.

Transmission electron microscopy (TEM) images were recorded on a JEOL 2100Plus transmission electron microscope. X-ray powder diffraction (XRD) measurements were performed on a Shimazu XRD-6100 diffractometer with Cu-Ka radiation (λ = 1.5406 Å) at 40kV and 30 mA. Fluorescence spectra were recorded on a Hitachi F-7000 instrument modified with a 980 nm laser. The UV-visible absorption measurements were performed on a U-2900 ultraviolet-visible spectrophotometer. Fluorescence lifetime decays were taken on Fluorolog-3 steady-state transient near-infrared microfluorescence spectrometer. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on INVENIO R（Bruker）FT-IR spectrometer. X-ray photoelectron spectroscopy measurements were performed on the X-ray photoelectron spectrometer (Thermo Fisher Scientific) using an unmonochromated Al KαX-ray source.

1.3 Synthesis of core-$NaYbF_4$ UCNPs

1 mmol $YbCl_3$, 9 mL OA and 10 mL ODE were added to 50 mL three-necked flask, and the clear solution was obtained by vacuum stirring at 120 °C for 1 h. After cooling to room temperature, 3.125 mmol of NaOA, 5 mmol of NH_4F, 3.125 mL of OM and 4.375 mL of ODE were added to the three-necked flask and stirred at vacuum room temperature for 30 min. Then, the reaction was rapidly heated to 315 °C in a nitrogen atmosphere for 45 min. After rapid cooling, ethanol was added to precipitate the nanoparticles, and centrifuged at 7500 rpm for 10 minutes to completely precipitate the nanoparticles to the bottom. For purification, the obtained nanoparticles were dispersed in 10 mL of n-hexane, precipitated with ethanol again, and collected by centrifugation. Finally, the nanoparticles were dispersed in 25 mL n-hexane and 50 μL oleic acid was added to maintain the long-term stability of the nanoparticles.

1.4 Synthesis of core-$NaYF_4$,2%Ho UCNPs

The synthesis process of the $NaYF_4$,2%Ho core was similar to the above process, but here 0.98 mmol YCl_3 and 0.02 mmol $HoCl_3$ were used instead of 1 mmol $YbCl_3$.

1.5 Preparation of shell precursor

Ln-OA: 3.5 mmol of $LnCl_3$ ($YbCl_3$, YCl_3 or $HoCl_3$, respectively), 14 mL OA and 21 mL of ODE were added to a 100 mL three-necked flask and stirred at 120 ° C for 2 h to obtain clear Ln-OA precursor solution with the concentration of 0.1 M.

Na-TFA-OA: 6 mmol Na-TFA and 15 mL OA were added to a 50 mL flask and stirred at vacuum room temperature until clarified to obtain a 0.4 M Na-TFA-OA precursor solution.

1.6 Synthesis of the core-shell $NaYbF_4$@$NaYF_4$:2%Ho and the core-shell-shell-$NaYbF_4$@$NaYF_4$:2%Ho@$NaYF_4$ core-shell-shell (CSS) UCNPs

The core-shell and core-shell-shell were synthesized by a successive layer-by-layer (SLBL) growth method, and the specific steps were as follows. 4 mL $NaYbF_4$ core nanoparticles, 4 mL OA and 6 mL ODE were added to a 50 mL three-necked flask and vacuumed at stirred at 70 °C for 45 min to remove n-hexane, oxygen and water. Subsequently, N_2 was introduced, and the temperature was increased to 300 °C for 5 min. Then the shell precursor solution was injected cyclically. Firstly, Ln-OA was injected. After 15 minutes, Na-TFA-OA was injected to end one cycle and immediately start the next cycle. The amount of precursor injected each time was shown in Table S1. After the last cycle, the solution was incubated for 30 min, then the solution was rapidly cooled to room temperature, and the nanoparticles were precipitated with ethanol. Then the precipitated nanoparticles were washed in the same manner as the core nanoparticles, and finally dispersed in 5 mL n-hexane, and 10 μL OA was added to maintain its long-term stability.

Note: The inner shell (e.g., $NaYF_4$:2%Ho) only required cycle 1-4 in Table S1. The total volume of the injected precursor was 2400 μL, including 1600 μL Ln-OA and 800 μL Na-TFA-OA. Fabricating the shell layer ($NaYF_4$) required cycle 5-8 in Table S1. The total volume of the injected precursor is 4690 μL, including 3120 μL Ln-OA and 1570 μL Na-TFA-OA. The volume of the injected Ln-OA shell precursor solution was allocated in proportion to the elements, and the total volume remained unchanged. The encapsulation process of $NaYF_4$:2%Ho@$NaYbF_4$@$NaYF_4$ (CSS (I)) and $NaYbF_4$@$NaYF_4$:20%Yb,2%Ho@ $NaYF_4$ (CSS (II)) is similar to that of CSS, only the type of precursors needs to be changed.

Table S1: Shell precursor injections.

Cycle Number	1	2	3	4	5	6	7	8
Ln-OA (μL)	280	360	440	520	620	720	830	950
Na-TFA-OA (μL)	140	180	220	260	310	360	420	480

1.7 Preparation of hydrophilic CSS UCNPs

Hydrophilic CSS UCNPs were obtained according to the method in the literature with some modifications. 5 mL CSS UCNPs dispersed in n-hexane and 50 mg $NOBF_4$ were dissolved in 5 mL DMF and stirred at room temperature for 30 min. Then the solid was collected by centrifugation at 12000 rpm for 10 min. The solid and 150 mg PAA were dispersed in 15 mL water and stirred at room temperature for 24 h. Next, the PAA-modified UCNPs were collected by centrifugation and washed with water, and finally dispersed into 5 mL of water.

1.8 Preparation of MnO_2-nanosheets-modified CSS UCNPs

MnO_2-nanosheets-modified nanoparticles were Prepared according to the method described by the literature. 200 μL PAA-modified UCNPs and 500 μL (0.1 M, pH = 6) MES solution was added to a 2 mL centrifuge tube, and then different volumes of 10 mM $KMnO_4$ solution were added. The mixed solution was ultrasonically treated for 30 min to form brown colloids. MnO_2-modified UCNPs were collected by centrifugation and washed with water, and finally dispersed in 2 mL of water.

1.9 AA detection

The 2 mL MnO_2-modified UCNPs were added to the cuvette, and then different concentrations of 2 μL AA solution were added successively. After shaking well, the fluorescence spectra under 980 nm excitation were recorded.

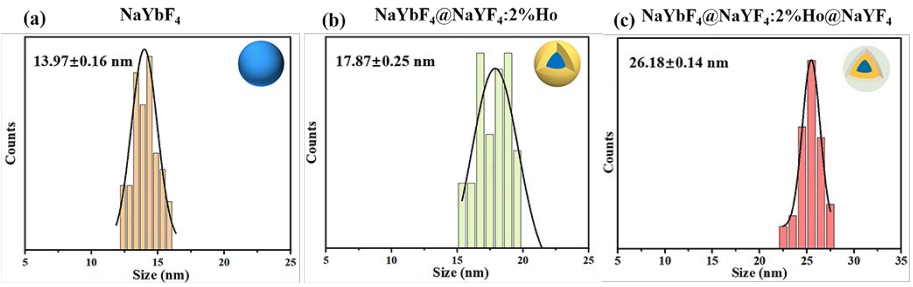

Figure S1. (a-c) The size distribution diagrams of the core, the core-shell and the core-shell-shell of $NaYbF_4$@$NaYF_4$:2%Ho@$NaYF_4$ (CSS), based on 130 individual particles.

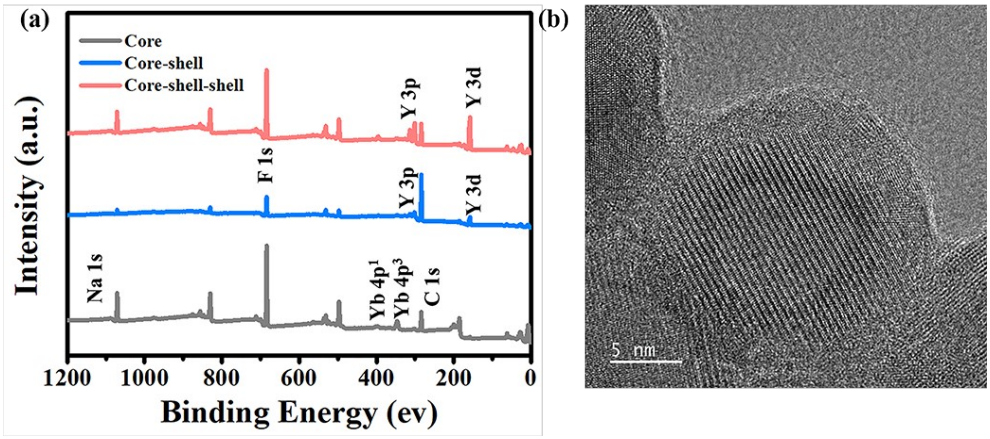

Figure S2. (a) XPS spectra of the core, the core-shell and the core-shell-shell of $NaYbF_4$@$NaYF_4$:2%Ho@$NaYF_4$ (CSS) and (b) TEM image of CSS.

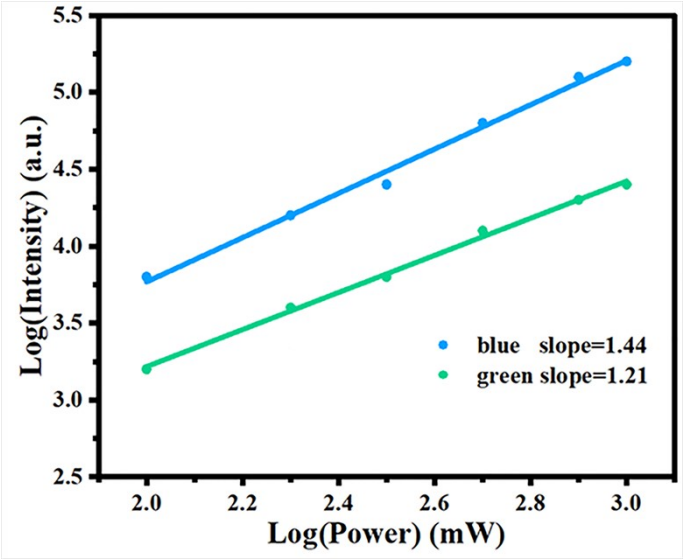

Figure S3. The dependence of upconversion luminescence intensity of blue and green emission bands on excitation power in CSS.

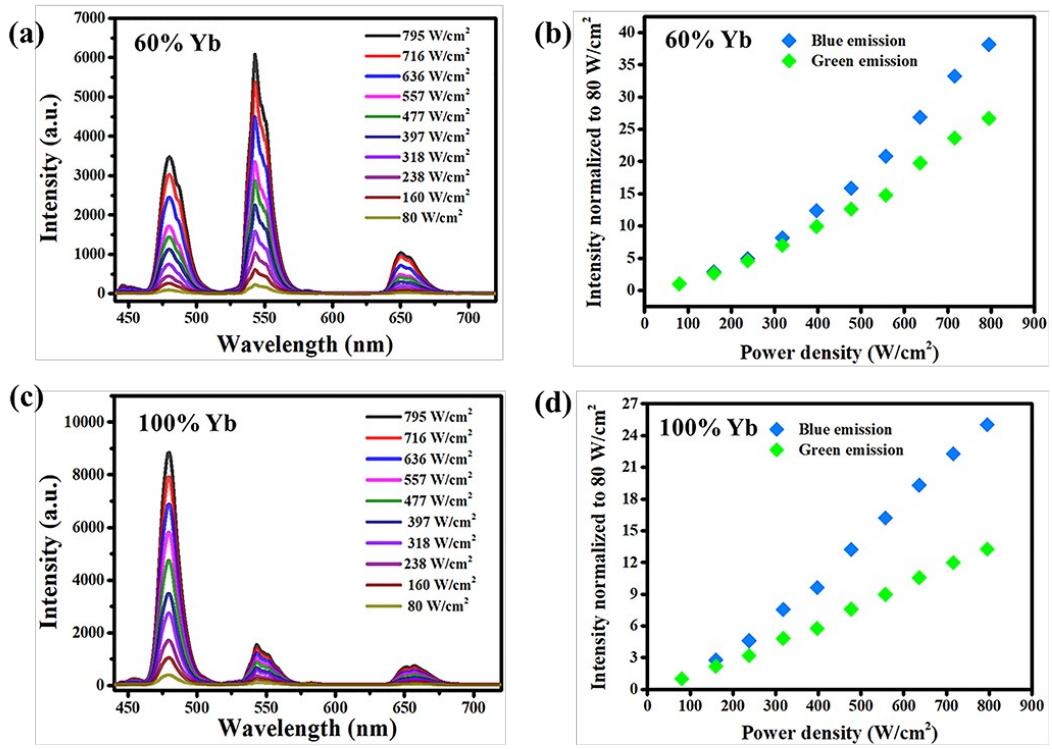

Figure S4. (a, c) Upconversion emission spectra and (b, d) variation trend of integrated intensity of CSS $NaYF_4$:x%Yb@$NaYF_4$:2%Ho@$NaYF_4$ (x = 60, 100) at different power density under 980 nm laser excitation (the concentration of 60% Yb and 100% Yb CSS UCNPs was 2 mg/mL and 85 μg/mL, respectively).

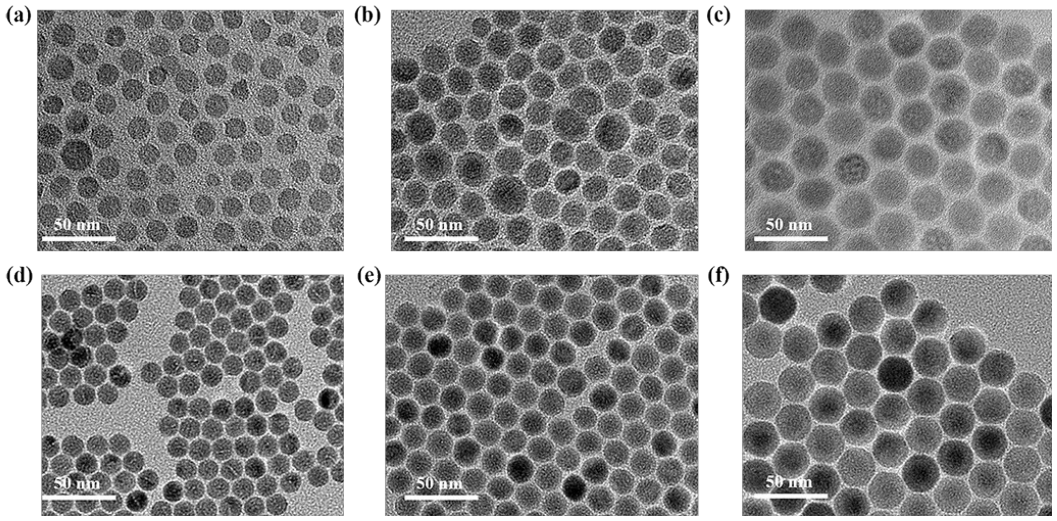

Figure S5 (a-c) TEM images of the core, the core-shell and the core-shell-shell of CSS (I) ($NaYF_4$:2%Ho@$NaYbF_4$@$NaYF_4$) and (d-f) of CSS (II) ($NaYbF_4$@$NaYF_4$:20%Yb,2%Ho@$NaYF_4$).

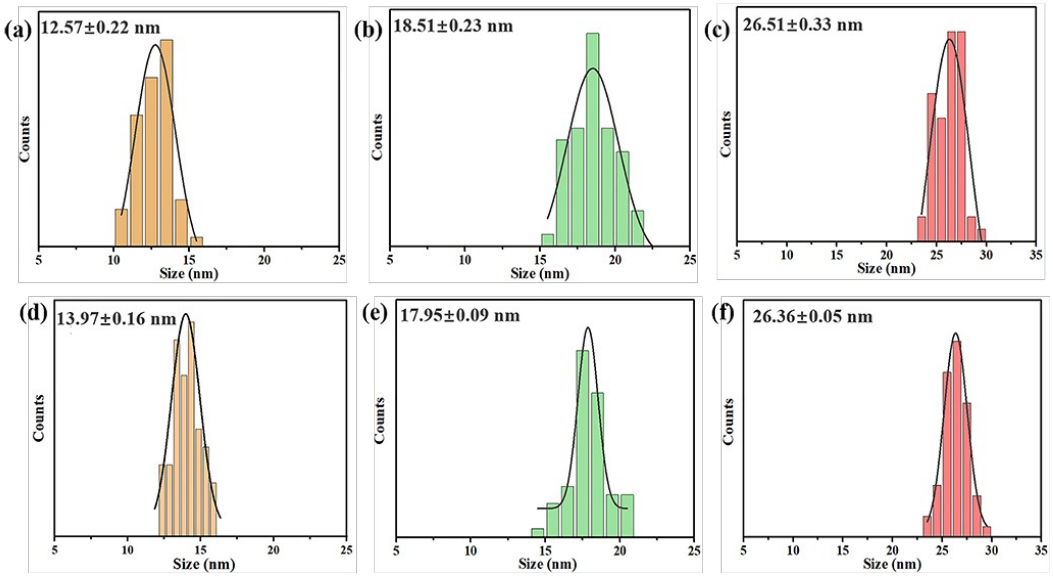

Figure S6. (a-c) Size distribution diagrams of the core, the core-shell and the core-shell-shell of CSS (I) ($NaYF_4$:2%Ho@$NaYbF_4$@$NaYF_4$) and (d-f) of CSS (II) ($NaYbF_4$@$NaYF_4$:20%Yb,2%Ho@$NaYF_4$), based on 130 individual particles.

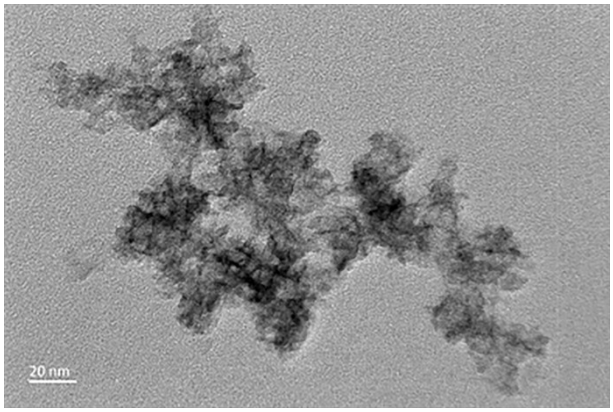

Figure S7. TEM image of MnO_2 nanosheets.

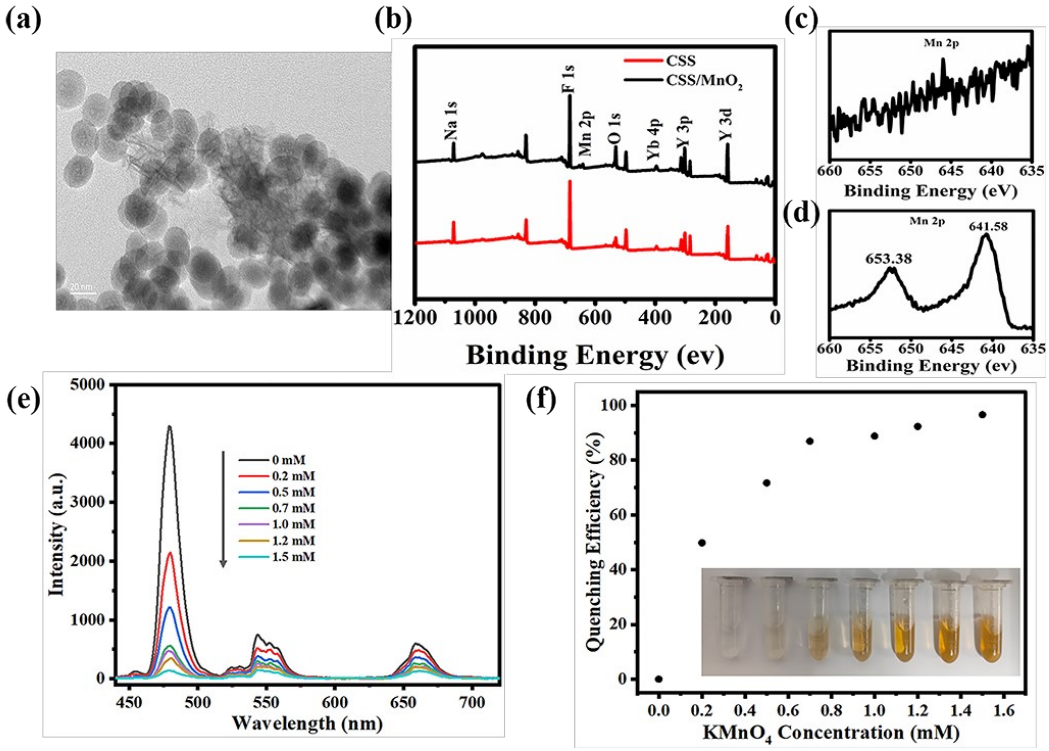

Figure S8. (a) TEM image of CSS/MnO_2. b) XPS spectra of CSS and CSS/MnO_2. (c) High resolution Mn (2p) XPS spectra of CSS. (d) High resolution Mn (2p) XPS spectra of CSS/MnO_2. (e) Upconversion emission spectra of CSS/MnO_2 assemblies formed at a series of different $KMnO_4$ concentrations. (f) Relationship between the fluorescence quenching efficiency of CSS/MnO_2 assemblied at 480 nm and the $KMnO_4$ concentration. Inset: Photographs of the CSS/MnO_2 UCNPs.

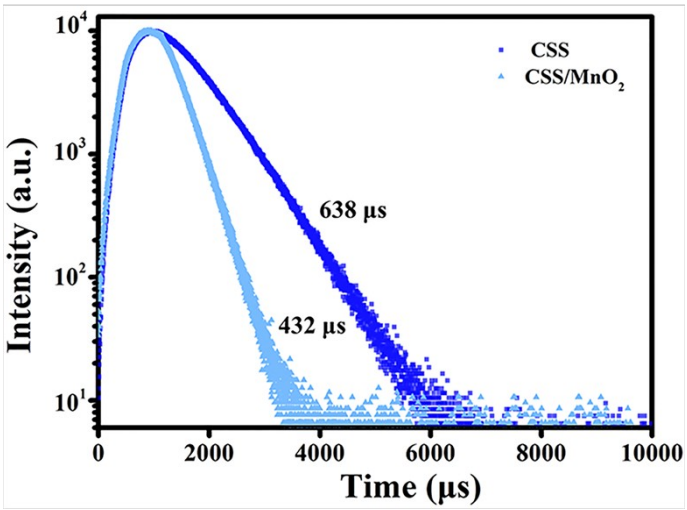

Figure S9. The decay lifetimes of CSS and CSS/MnO_2.

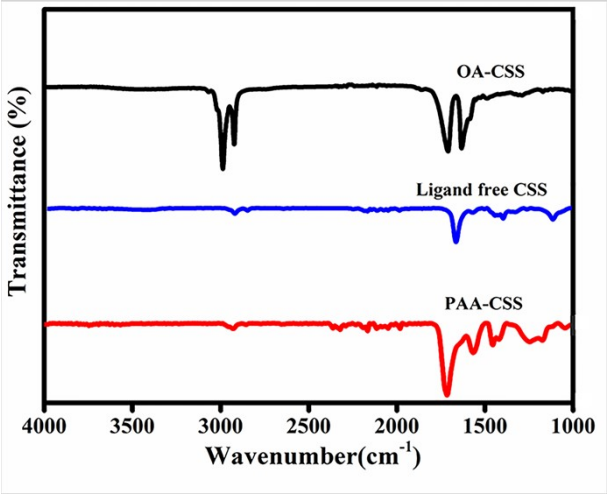

Figure S10. FT-IR spectra of OA-coated (top, black), ligand-free (middle, blue) and PAA-modified (bottom, red) CSS.

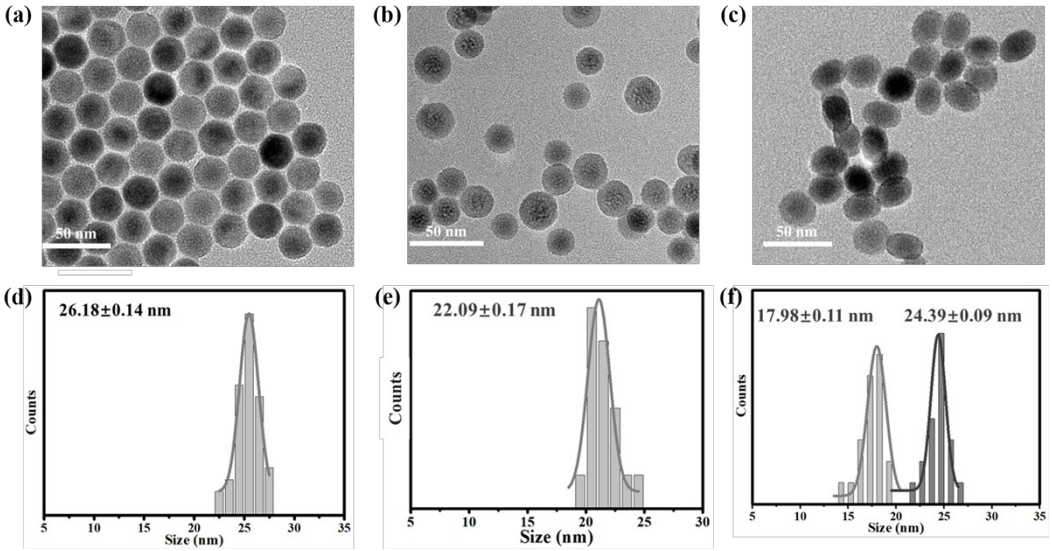

Figure S11. (a, d) TEM images size and distribution diagrams of OA-coated, (b, e) ligand-free and (c, f) PAA functionalized CSS.

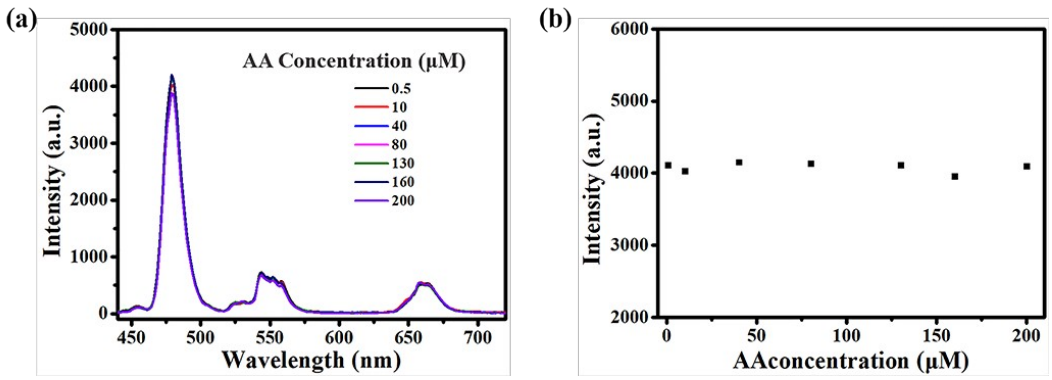

Figure S12. (a) The fluorescence spectra and (b) intensity corresponding to different concentrations of AA added to the CSS solution.

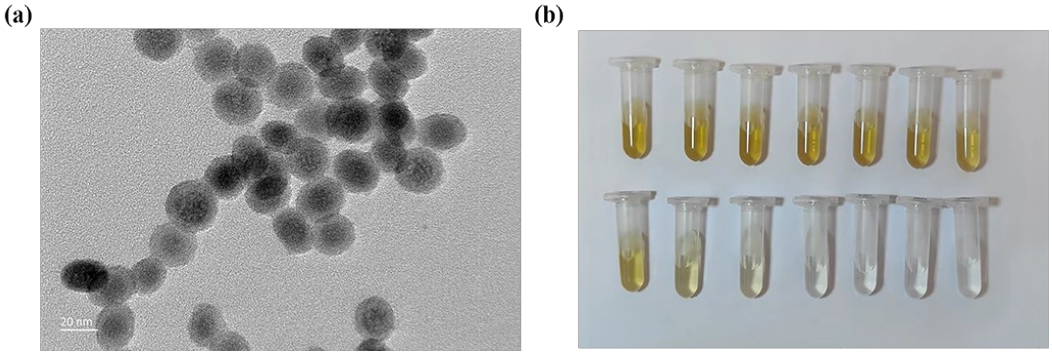

Figure S13. (a) TEM image of CSS/MnO_2 with AA concentration of 130 μM. (b) A series of photographs of CSS/MnO_2 aqueous solution with different AA concentrations (0-200 μM).

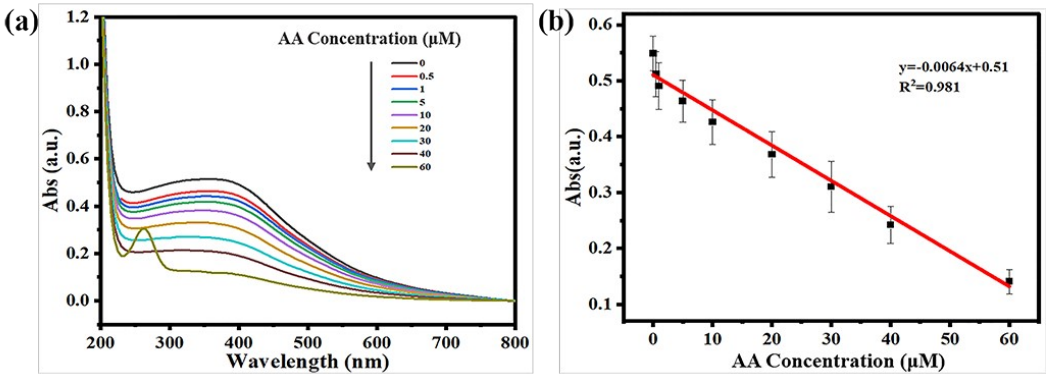

Figure S14. (a) UV absorption spectra of MnO_2 with different concentrations of AA (0-60 μM). (b)The UV absorption intensity of MnO_2 at 350 nm varies with AA concentration (0-60 μM). Error bars indicate the standard deviations of three repetitive experiments.

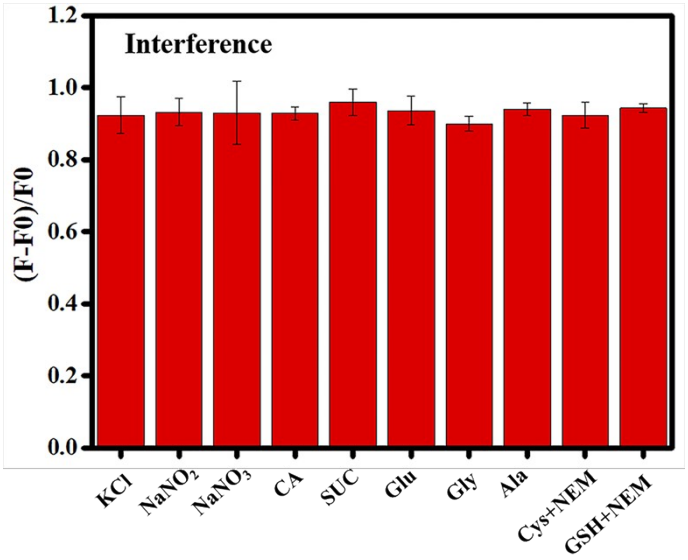

Figure S15. Anti-interference test of CSS/MnO_2.The concentration of other interfering substances (KCl, $NaNO_2$, $NaNO_3$, CA, SUC, Glu, Gly, Ala, Cys and GSH) was 300 μM, NEM was 900 μM, and AA was 30 μM. Error bars indicate the standard deviations of three repetitive experiments.

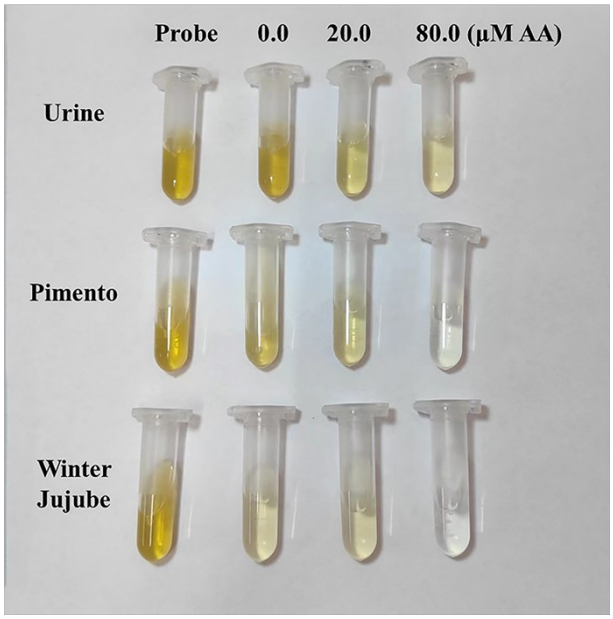

Figure S16. The color change of CSS/MnO_2 in urine, pimento and winter jujube after adding 0.0, 20.0 and 80.0 μM AA solution, respectively.