Supplementary Information

Size-dependent modulation of fluorescence and light scattering: a new strategy for development of ratiometric sensing

Shi Gang Liu [a], Na Li [a], Lei Han [a], Ling Jie Li [b], Nian Bing Li [a]*, and Hong Qun Luo [a]*

[a] Key Laboratory of Eco–environments in Three Gorges Reservoir Region (Ministry of Education), School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, People's Republic of China

[b] School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, People's Republic of China

Corresponding Author. E-mail address: linb@swu.edu.cn (NB Li); luohq@swu.edu.cn (HQ Luo).

Experimental section

Materials. Citric acid, acetic acid (HAc), sodium acetate (NaAc), sodium hypochlorite (NaClO), $CoCl_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, and $Fe(NO_3)_3 \cdot 9H_2O$ were obtained from Chengdu Kelong Chemical Reagent Plant (Sichuan, China). Hyperbranched polyethyleneimine (PEI, M_w = 600), hydrogen tetrachloroaurate hydrate ($HAuCl_4 \cdot 4H_2O$), and L-glutathione (GSH) were purchased from Aladdin Ltd., Shanghai, China. Other reagents were of analytical reagent grade, and all the chemicals were used without further purification. Ultrapure water (18.2 MΩ cm) was used throughout the experiment. HAc-NaAc buffer (0.1 M) was prepared according to the standard protocol.

Instruments. The fluorescence and light-scattering spectra were collected on an F-2700 spectrofluorometer (Hitachi, Japan). The slits of both excitation and emission were fixed at 10 nm, and the photomultiplier tube (PMT) voltage was set at 400 V. UV-vis absorption spectra were recorded using a UV-vis 2450 spectrophotometer (Shimadzu, Japan). A KQ-250B ultrasonic bath (Kun Shan Ultrasonic Instruments Co., Ltd, China) was used to prepare CoOOH nanoflakes. Transmission electron microscopy (TEM) measurement was carried out with a JEM 1200EX transmission electron microscope (JEOL, Japan). Atomic force microscopy (AFM) characterization was performed on a Dimension Icon10800 atomic force microscope (Bruker, Germany). A PHS-3C pH meter (Shanghai Leici Instrument Company, Ltd., China) was utilized to detect pH values of solutions.

Preparation of CoOOH Nanoflakes. CoOOH nanoflakes were prepared

according to a previously reported method with minor modification.[1-3] Briefly, 300 μL of NaOH solution (1.0 M) was added to a vial and mixed with 1.0 mL of $CoCl_2$ solution (10 mM). After sonicating for 5 min, the mixture was centrifuged at 12,000 rpm for 10 min and the precipitate was obtained and redispersed in 1.0 mL of ultrapure water. Then, 50 μL of 0.9 M sodium hypochlorite solution was added, and the mixture was sonicated for 20 min. Subsequently, the resulting CoOOH nanoflake solution was centrifuged at 12,000 rpm for 10 min and the precipitate was obtained and washed three times with ultrapure water, and finally dispersed in 2.0 mL of ultrapure water.

Preparation of Carbon Dots. CDs were prepared in accordance with a published report with a slight change.[4] Typically, PEI (0.05 g) and citric acid (0.25 g) were dissolved in 5.0 mL of ultrapure water with ultrasonic treatment. The mixture was then transferred to a 25 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 2 h. After the reactor cooled down to room temperature naturally, the resulting solution was centrifuged at 2, 000 rpm for 10 min to remove large particles, and then the supernatant was dialyzed against water for 24 h through a dialysis film. The product inside the dialysis bag was lyophilized and redispersed in ultrapure water. The CDs solution with blue fluorescence was obtained.

Procedures for Sensing Ascorbic Acid. For AA ratiometric sensing by fluorescence and second-order scattering, the CDs/CoOOH nanoflakes system and sensing procedure are described as follows. 1.0 mL of CoOOH nanoflakes (8.0 mg mL^{-1}) and 250 μL of CDs (2 mg mL^{-1}) were mixed with 8.75 mL of ultrapure water.

The mixture was sonicated for 10 min, and then, the CDs/CoOOH nanoflakes system as the standardized sensing platform was prepared. To evaluate the sensitivity, 200 μL of CDs/CoOOH nanoflakes was added to 700 μL of HAc-NaAc buffer (0.1 M, pH 5.0), and the solution was mixed. Then 100 μL of AA solution with various concentrations was added to the mixtures, followed by shaking well. The mixtures were equilibrated for 30 min before spectral measurements. At last, the fluorescence and scattering spectra were recorded under excitation at 350 nm. All measurements were carried out at room temperature. For sensing by using SODL-fluorescence, first-order scattering, and frequency doubling scattering, the CDs/CoOOH nanoflakes system was prepared by mixing 1.0 mL of CoOOH nanoflakes (8.0 mg mL^{-1}) and 250 μL of CDs (50 mg mL^{-1}) in 8.75 mL of ultrapure water, and fluorescence and scattering spectra were recorded under excitation at 700 nm. Other procedures were the same as described above.

Preparation of Ag Nanoparticles. Ag NPs were prepared by the well-known citrate reduction method.[5] Typically, 50 mL of $AgNO_3$ solution (1 mM) was heated under gentle stir until it began to boil. Then, 2 mL of trisodium citrate (1%, w/v) was introduced dropwise to the $AgNO_3$ solution. With continuous stirring, the mixed solution was boiled for an additional 15 min. Subsequently, the solution was cooled to room temperature and the resulting Ag NP solution with brown yellow was obtained.

Procedures for ratiometric detection of H_2O_2. For H_2O_2 ratiometric sensing by combined fluorescence and SOS, the sensing procedures are described as follows. Quinine sulfate (100 μL, 0.48 μM), Ag NPs (200 μL), and 100 μL of PBS buffer (1/15

M, pH 6.5) were added to 500 μL of water, and the solution was mixed. Then 100 μL of H_2O_2 solution with various concentrations was added to the mixture, followed by shaking well. The mixed solutions were incubated at 60 ºC for 20 min before spectral measurements. At last, the fluorescence and SOS spectra were collected under excitation at 330 nm.

Preparation of Glutathione-Protected Gold Nanoclusters. GSH-protected Au NCs were synthesized according to Xie's reported method.[6] Typically, freshly prepared 0.50 mL of $HAuCl_4$ solution (20 mM) and GSH (100 mM, 0.15 mL) were mixed with 4.35 mL of ultrapure water. Then, the reaction mixture was heated at 70 °C for 24 h under gentle stirring. After the resulting light-yellow solution was centrifuged at 2,000 rpm for 10 min to remove large particles, an Au NCs aqueous solution with strong orange emission was formed.

Investigation of Metal Ions-Induced Fluorescence Quenching. A 100 μL amount of the as-synthesized GSH-Au NCs was mixed with 800 μL of HAc-NaAc buffer (0.1 M, pH 5.0). Then, 100 μL of Fe^{3+} or Cu^{2+} solution with various concentrations was added to the mixture, followed by shaking well. After 5 min, the fluorescence and scattering spectra were recorded under excitation at 365 nm. All measurements were performed at room temperature.

Additional figures

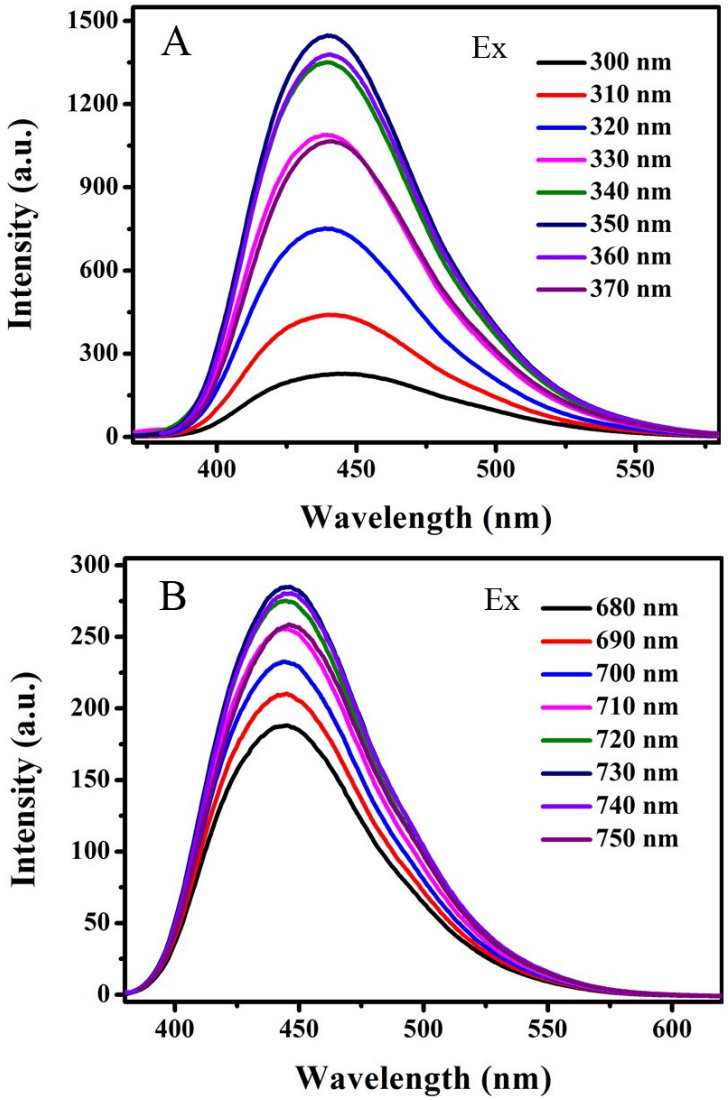

Fig. S1. Down-conversion fluorescence (20 mg L^{-1}) (A) and SODL-fluorescence (500 mg L^{-1}) (B) spectra of CDs under different excitations.

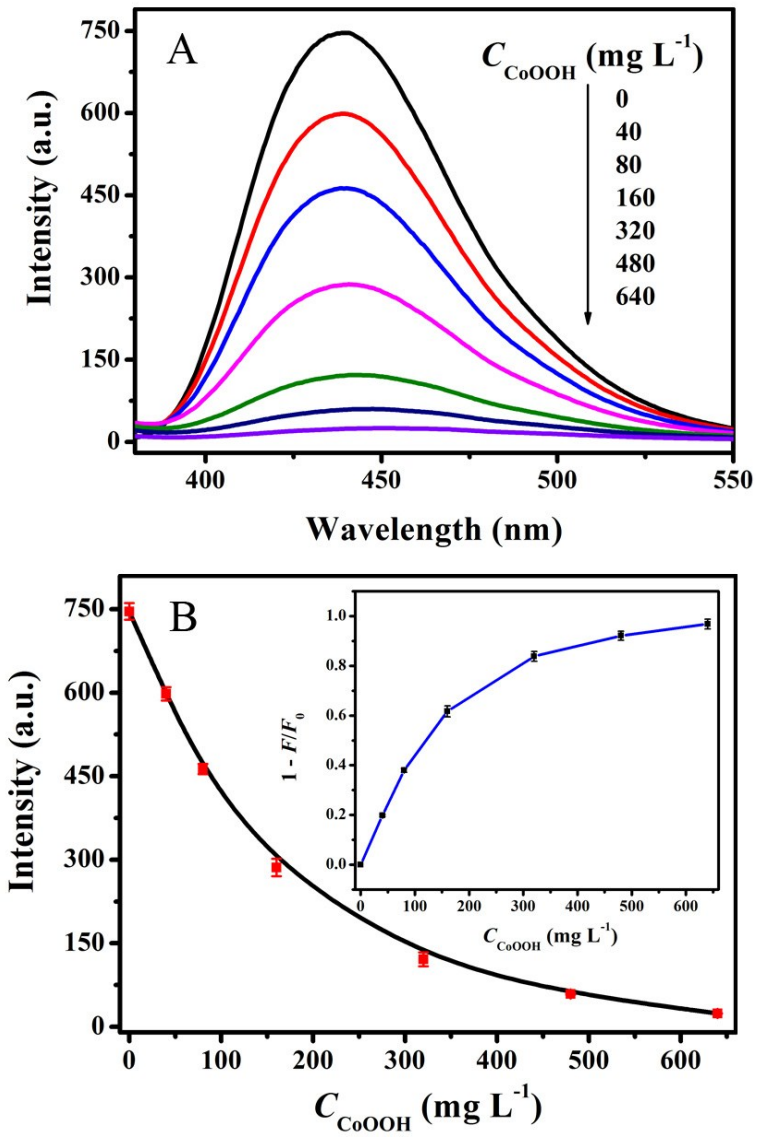

Fig. S2. Fluorescence quenching ability of CoOOH nanoflakes. (A) Fluorescence emission spectra and (B) fluorescence intensities at 445 nm as a function of increasing CoOOH nanoflake concentration. Inset of (B) is a relationship between quenching efficiency (1 - F/F_0) and CoOOH nanoflake concentration, where F and F_0 denote the fluorescence intensity in the presence and absence of CoOOH nanoflakes, respectively. Conditions: excitation, 350 nm; CDs, 10 mg L^{-1}; NaAc-HAc buffer (pH 5.0).

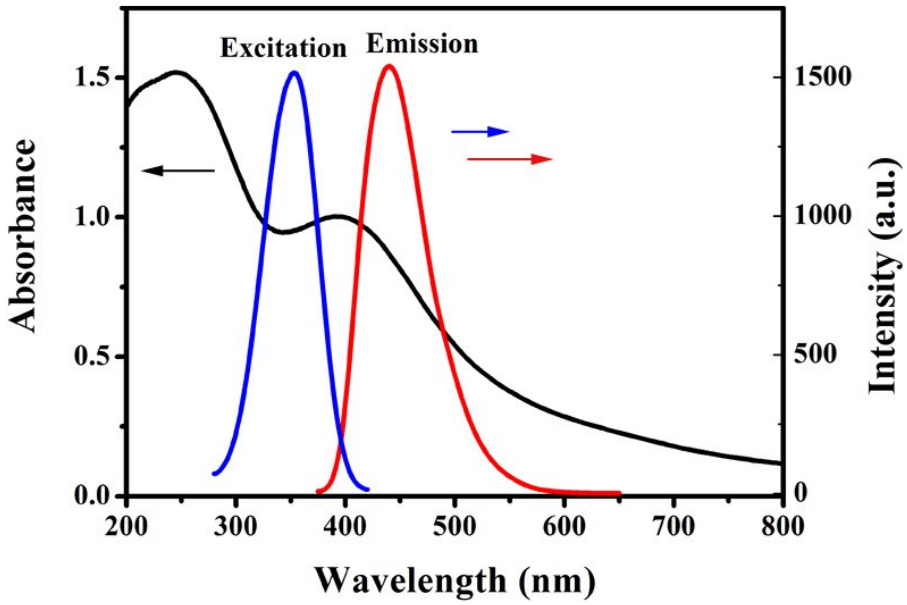

Fig. S3. UV-vis absorption spectrum of CoOOH nanoflakes (400 mg L^{-1}, black curve), down-conversion fluorescence excitation (blue curve) and emission spectra (red curve) of the CDs (20 mg L^{-1}).

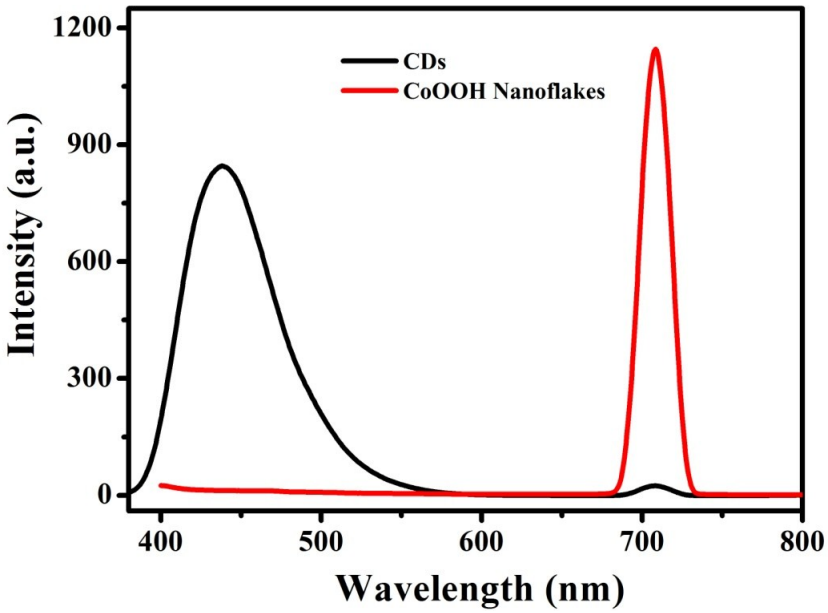

Fig. S4. SOS spectrum of CoOOH nanoflakes (red curve) down-conversion fluorescence and SOS spectrum of CDs (black curve). Both excitations are 350 nm. CDs, 10 mg L^{-1}; CoOOH nanoflakes, 160 mg L^{-1}.

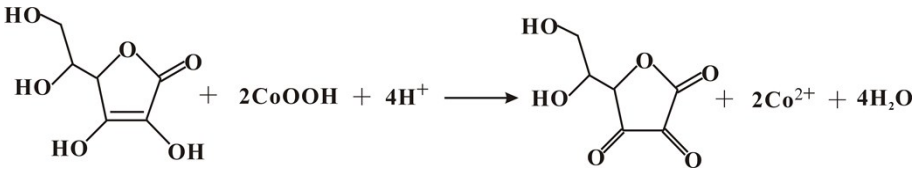

Fig. S5. The reaction scheme of AA with CoOOH. [1-3]

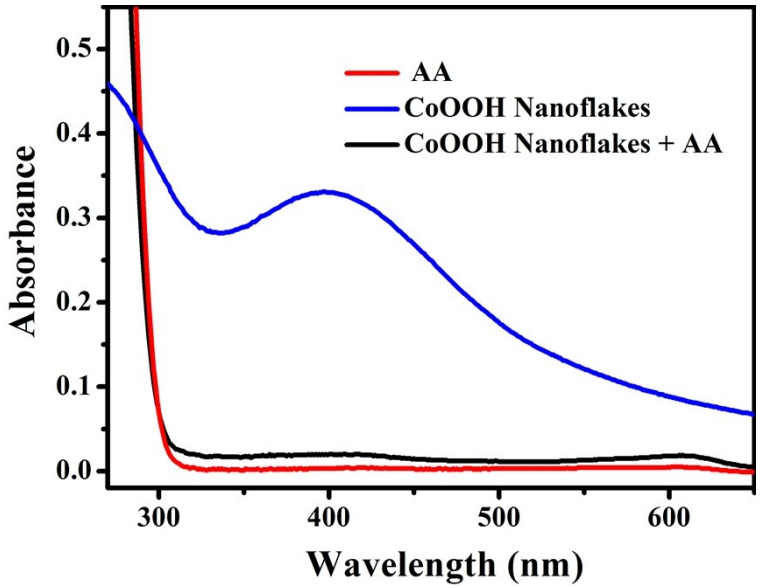

Fig. S6. UV-vis absorption spectra of CoOOH nanoflakes (160 mg L^{-1}) in the absence and presence of AA (200 μM).

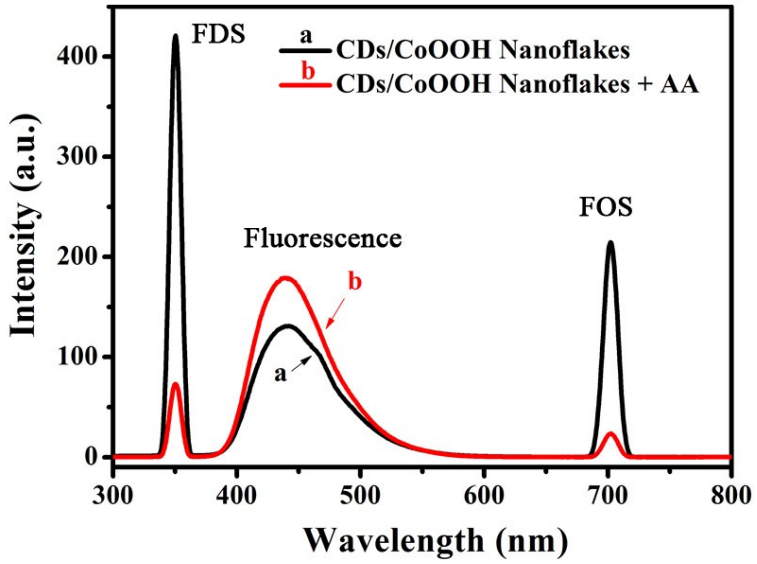

Fig. S7. SODL-fluorescence, FOS, and FDS spectra of CoOOH nanoflakes in the absence (curve a) and presence of AA (curve b). Conditions: CDs, 250 mg L^{-1}; CoOOH nanoflakes, 160 mg L^{-1}; AA, 200 μM; HAc-NaAc buffer (pH 5.0); excitation, 700 nm.

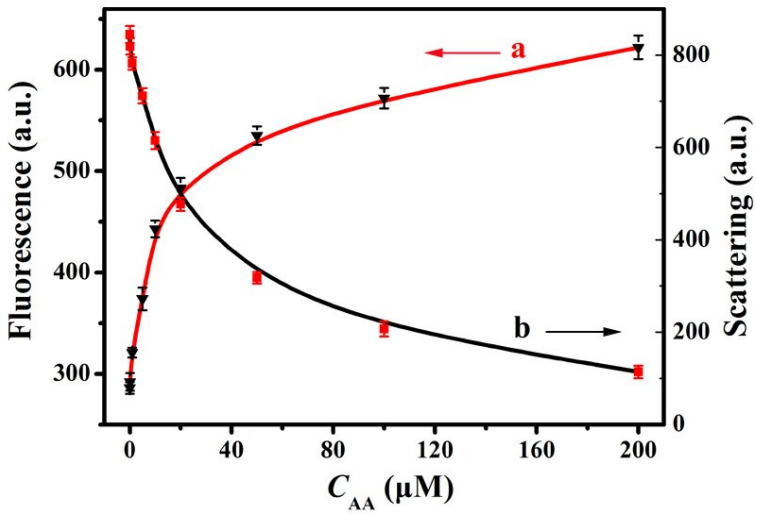

Fig. S8. Fluorescence intensity at 445 nm (curve a) and SOS intensity at 708 nm (curve b) changes of the CDs/CoOOH nanoflakes system in the presence of various concentrations of AA. Conditions: CDs, 10 mg L^{-1}; CoOOH nanoflakes, 160 mg L^{-1}; HAc-NaAc buffer (pH 5.0); excitation, 350 nm.

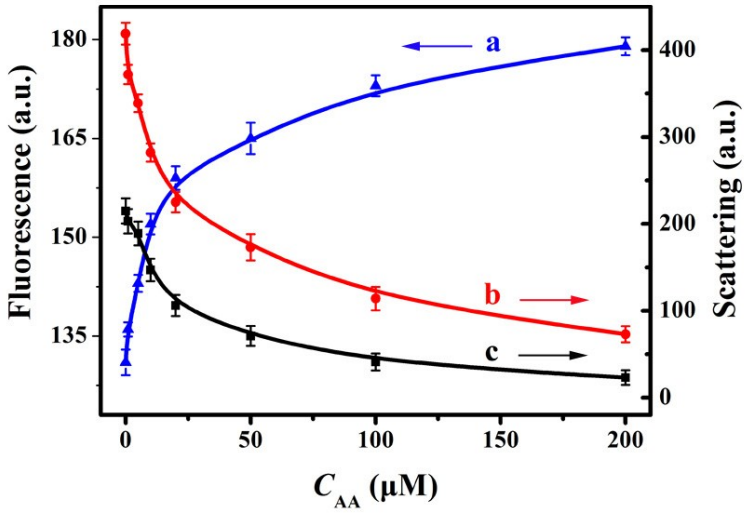

Fig. S9. SODL-fluorescence intensity (445 nm, curve a), FOS intensity (702 nm, curve c), and FDS intensity (350 nm, curve b) changes of the CDs/CoOOH nanoflakes system in the presence of various concentrations of AA. Conditions: CDs, 250 mg L^{-1}; CoOOH nanoflakes, 160 mg L^{-1}; HAc-NaAc buffer (pH 5.0); excitation, 700 nm.

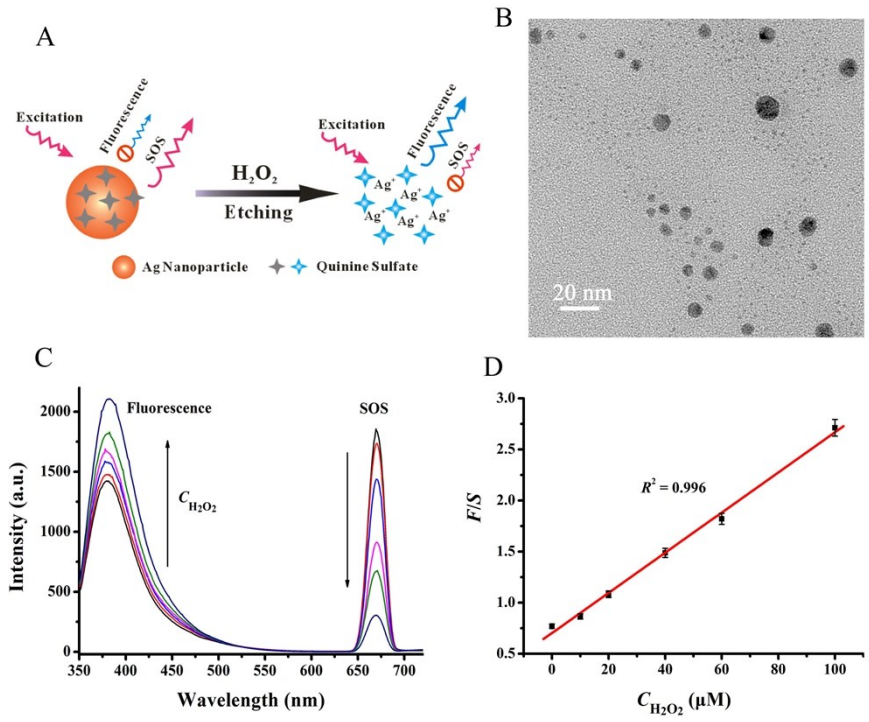

Fig. S10. (A) Schematic depiction of quinine sulfate/Ag NPs-based ratiometric optical sensor of H_2O_2 by the combination of fluorescence and SOS. (B) TEM image of Ag NPs. (C) Fluorescence and SOS spectra of quinine sulfate/Ag NPs hybrid system after adding various concentrations of H_2O_2 (0, 10, 20, 60, 100, 200 μM). Excitation, 330 nm; PBS buffer, pH 6.5; quinine sulfate, 48 nM; Ag NPs, 200 μL mL^{-1}. (D) Plot of linear relationship of F/S (where F and S denote fluorescence and SOS intensity, respectively) versus the concentrations of H_2O_2 ranging from 0 to 100 μM.

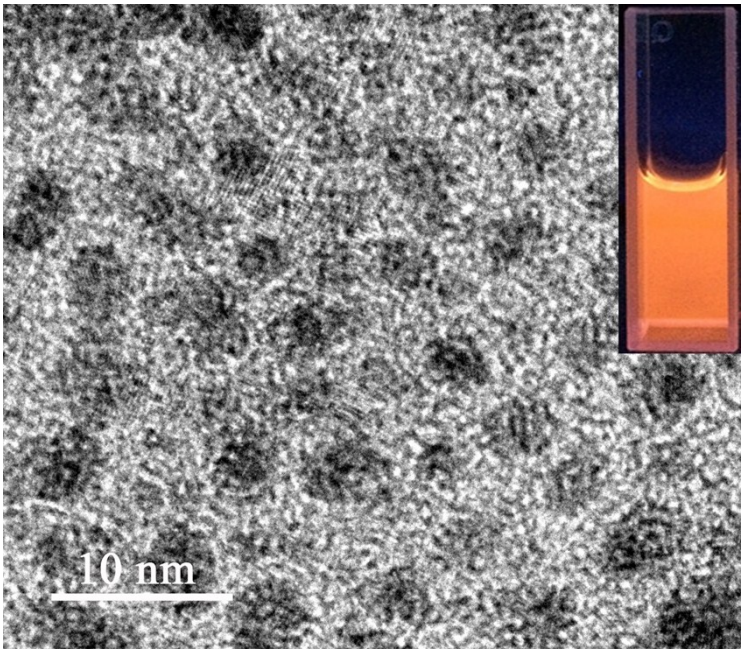

Fig. S11. TEM image of Au NCs and inset is a photograph of Au NCs under 365 nm UV light.

Supplementary References

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