Supporting Information

Dual-Functional Au-Fe_3O_4 Dumbbell Nanoparticels for Sensitive and Selective Turn-on Fluorescent Detection of Cyanide Based on the Inner Filter Effect

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Experimental Section

Materials: 1-octadecene, oleic acid, oleylamine were purchased from Sigma–Aldrich. Rhodamine B, $HAuCl_4 \cdot 3H_2O$, potassium cyanide, hexadecyl trimethyl ammonium bromide (CTAB) and other salts were purchased from Beijing Chemical Co. (China). All other chemicals were of analytical grade, and used without further purification. The water used was purified through a Millipore system.

Preparation of Au NPs: A solution of 1-octadecene (10 mL), oleic acid (1 mL), oleylamine (1 mL) and $HAuCl_4 \cdot 3H_2O$ (60mg) were prepared in air at room temperature. The mixture was allowed to be kept at 130°C for 30min with magnetically stirred and the color of the solution changed from light yellow to deep purple. Then the solution was cooled to room temperature. Ethanol was added to precipitate the Au NPs. The Au NPs were collected by centrifugation, washed with hexane, and redispersed in hexane.

Preparation of Au-Fe_3O_4 dumbbell NPs: Fe-oleate was prepared according to the reported method.[1] 1-octadecene (8 mL), oleic acid (1 mL), oleylamine (1.5 mL), 0.25g Fe-oleate and the Au NPs were mixed with magnetically stirred and degassed under a nitrogen flow for 60 min. Then the solution was heated to 320°C and kept for 40 min before it was cooled to room temperature. The mixture was exposed to air for one hour to ensure the formation of Fe_3O_4. Ethanol was added to precipitate the product, followed by centrifugation. The precipitated products were washed by hexane, and this process was repeated for two times.

Preparation of water-soluble Au-Fe_3O_4 dumbbell NPs: The Au-Fe_3O_4 NPs were dried under vacuum and added into the NaOH-Na_2HPO_4 buffer (0.01M, PH=10.5) containing 0.05 M CTAB. After 15 min sonication, the products dissolved and formed a purple red solution.

Turn-on fluorescent detection of cyanide: A 0.12 M stock solution of KCN was prepared in a NaOH-Na_2HPO_4 buffer (0.01 M, pH 10.5), from which various CN^- concentrations were prepared by serial dilution. A freshly prepared mixture solution containing 6.0×10^{-7} M RB and ca. 12mg Au/L as-prepared Au-Fe_3O_4 NPs (the concentration of NPs was obtained from ICP) in NaOH-Na_2HPO_4 buffer (0.01 M, pH 10.5) was used for CN^- detection, into which KCN with different concentrations was added. The kinetics of the interaction between cyanide and Au NPs showed that the reaction carried out rapidly in the first several minutes and slowly later. Thus the mixture solution was equilibrated for a fixed time of 30 min before separation by the magnet. Four-fifths of the supernatant was removed and the remaining was dispersed under ultrasonic for spectral measurements. It is worth noting that to avoid the loss of nanoparticles as much as possible is very important in the process of magnetic concentration. Better results can be achieved if the Au-Fe_3O_4 NPs used were separated first by the magnet in the synthesis procedure, and care is needed to keep the tip of the pipette not too close to the materials absorbed on the side of the container during the concentration.

The selectivity of this method was evaluated by testing the fluorescence response of this system to other common anions using the following salts: Na_2S, KSCN, NaBr, $KBrO_3$, Na_2CO_3, NaCl, $NaClO_4$, $NaNO_3$, Na_2SO_4, Na_2SO_3, KCN, CH_3COONa (NaAc), Na_3PO_4, $NaNO_2$, $NaIO_3$, sodium citrate, $Na_2C_2O_4$, NaF and NaI. The salt solutions above were mixed with the solution containing RB and Au-Fe_3O_4 NPs in a NaOH-Na_2HPO_4 buffer (0.01 M, pH 10.5) and equilibrated for 30 min before the spectral measurements.

Detection of cyanide in real samples: The tap water and ground water samples were used without any pretreatment. The lake water sample was filtered twice using filter papers (pore diameter 220nm). For lake water sample containing the dyes, 0.18μM RB or 2.0μM MB solution was prepared using lake water. Each water sample spiked with cyanide was used for preparation of the fluorescence detection system.

Instruments: Absorption measurements were performed with a Cary 500 UV-vis-NIR spectrometer (Varian). Fluorescence measurements were carried out on a LS-55 luminescence spectrometer (Perkin-Elmer), using a 1.00 cm path length rectangular quartz cell, and 535nm was used as the excitation wavelength for the fluorescence detection. TEM measurements were made on a HITACHI H-8100 EM with an accelerating voltage of 200 kV and a FEI-TECNAI G^2 transmission electron microscope operating at 200 kV. X-ray diffraction (XRD) analysis was carried out on a D/Max 2500 V/PC X-ray diffractometer using Cu (40 kV, 30 mA) radiation. Magnetic measurements were carried out using a superconducting quantum interference device (SQUID) magnetometer (LakeShore 7307) at 300K. The SQUID measurements for all the samples were done on the pure and dried powders. Element analysis was carried out on an ICP spectrometer (ICAP 6000 Series, Thermo Scientific). Zeta potential measurements were performed using a Zeta sizer NanoZS (Malvern Instruments).

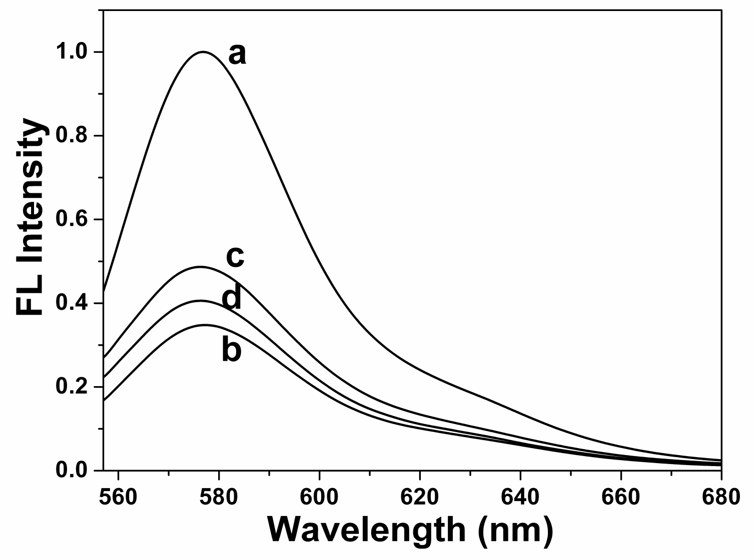

Fig. S1 Fluorescence emission spectra of 6.0×10^{-7}M RB (a); RB solution containing 60mg Au/L Au-Fe_3O_4 NPs (b); fluorescence recovery for detection of the same concentration of KCN with (c) and without the magnetic concentration process (d).

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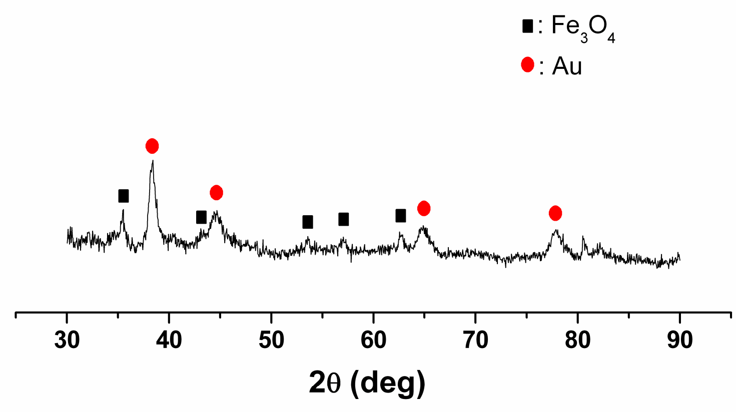

Fig. S2 XRD of the Au-Fe_3O_4 NPs.

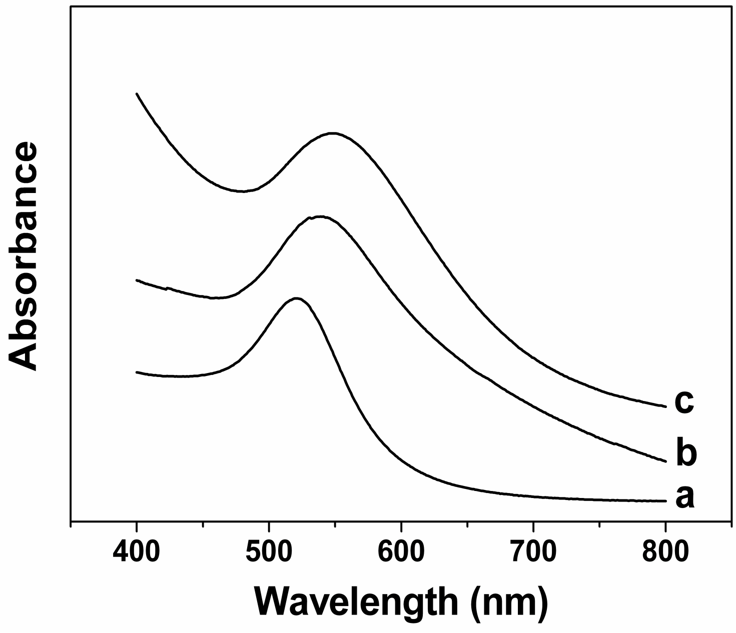

Fig. S3 a) Absorption spectra of Au NPs in the hexane; b) Au-Fe_3O_4 NPs in the hexane and c) Au-Fe_3O_4 NPs in the water.

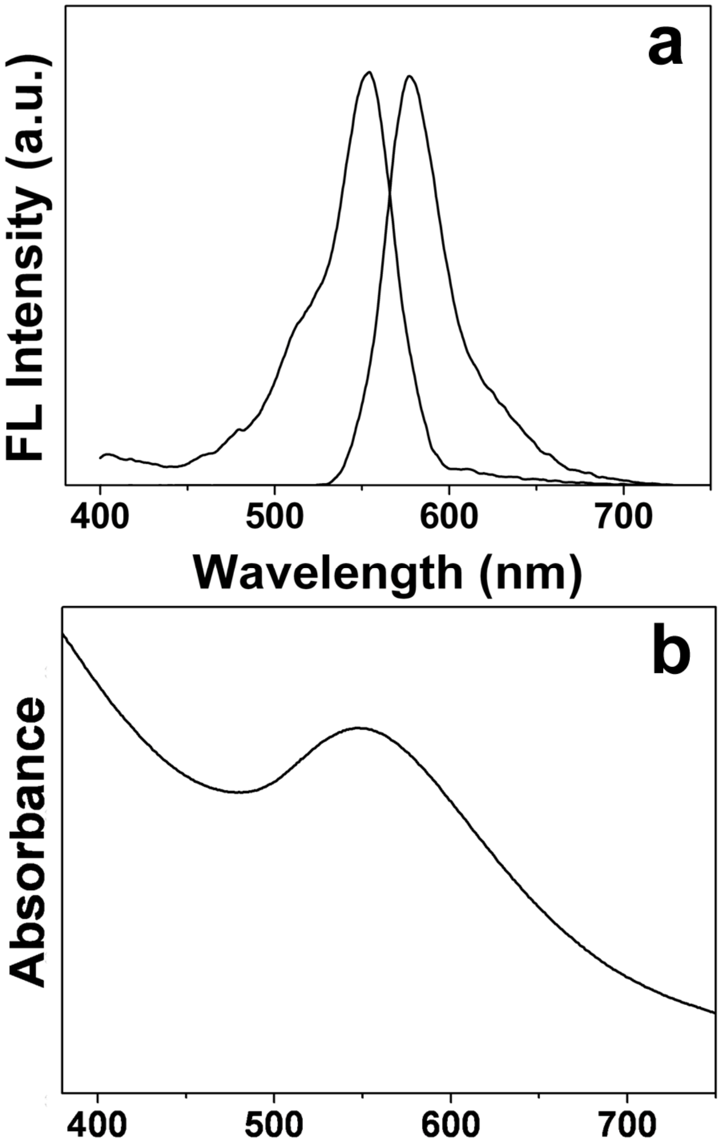

Fig. S4 a) Fluorescence excitation and emission spectra of RB and b) absorption spectrum of as-prepared Au-Fe_3O_4 NPs in NaOH-Na_2HPO_4 buffer (0.01 M, pH 10.5).

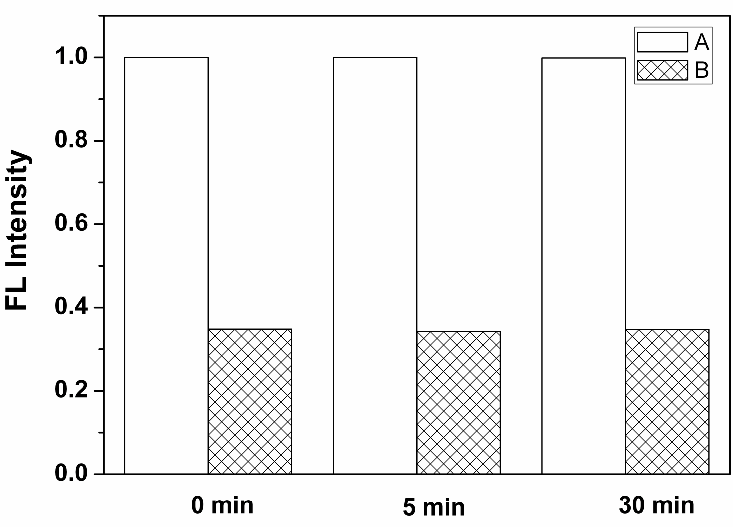

Fig. S5 A) Fluorescence intensity of Rhodamine B in the buffer containing CTAB over time and B) containing CTAB and Au-Fe_3O_4 NPs.

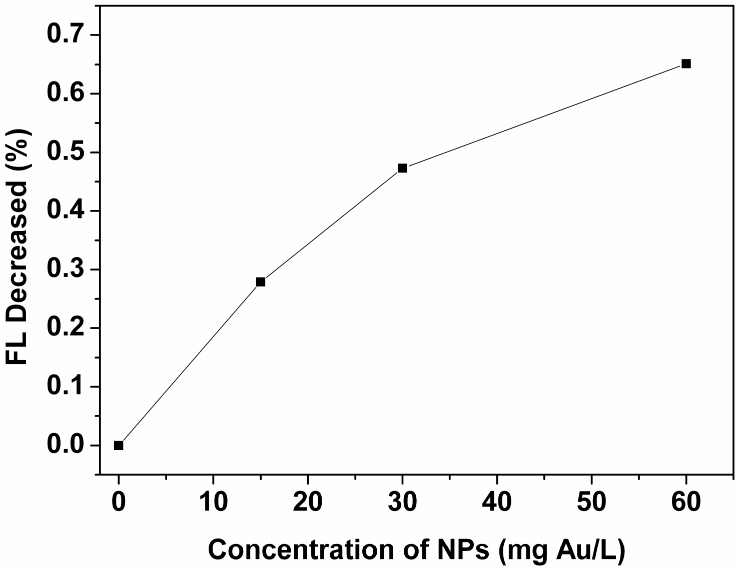

Fig. S6 Decreased fluorescence intensity (%) of Rhodamine B at 577 nm versus the concentration of Au-Fe_3O_4 NPs.

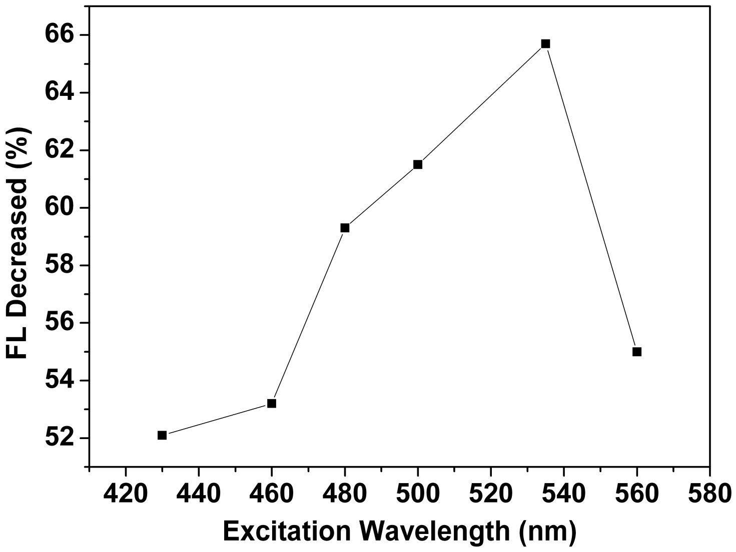

Fig. S7 The plots of fluorescence decreased (%) at 577 nm versus the excitation wavelength.

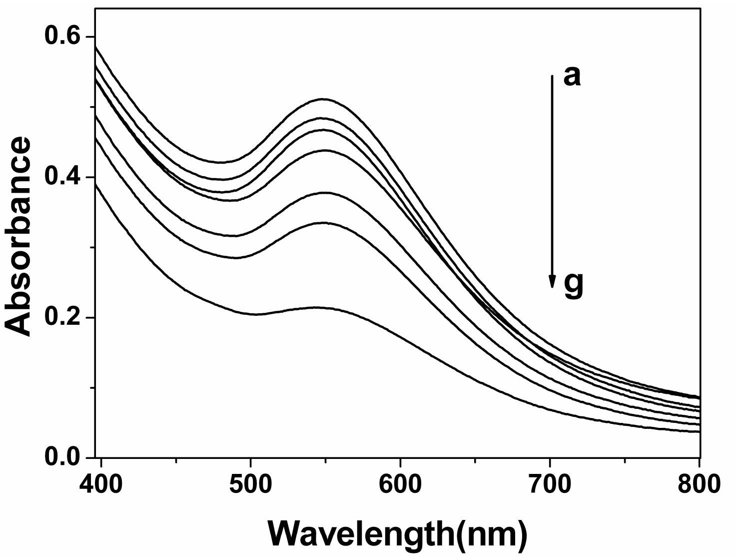

Fig. S8 Absorption spectra of Au-Fe_3O_4 NPs in the presence of increasing cyanide concentrations: a) 0M, b) 1.0×10^{-5} M, c) 2.5×10^{-5} M, d) 5.0×10^{-5} M, e) 7.5×10^{-5} M, f) 1.0×10^{-4} M, g) 2.0×10^{-4} M.

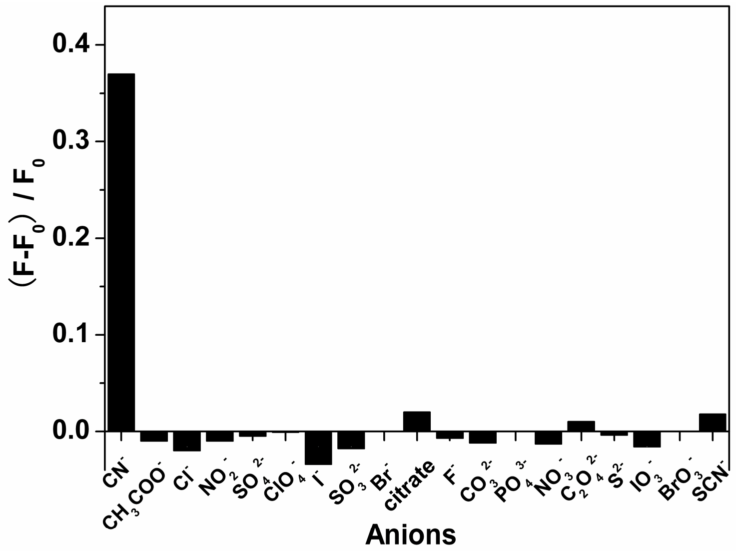

Fig. S9 The fluorescence response of the mixture solution containing RB (6.0×10^{-7}M) and Au-Fe_3O_4 NPs (ca. 60 mg Au/L) in NaOH-Na_2HPO_4 buffer (0.01 M, pH 10.5) at 577 nm in the presence of 2.0×10^{-4}M various anions.

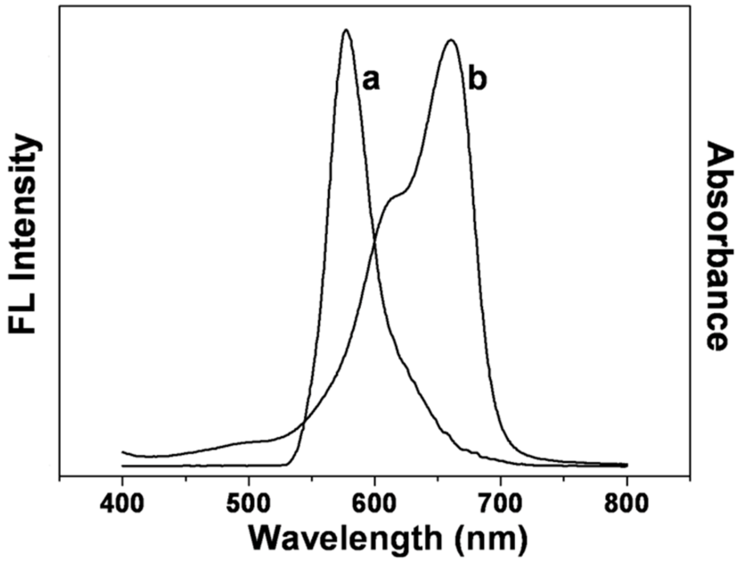

Fig. S10 a) Fluorescence emission spectra of RB and b) UV-vis absorption spectra of the methylene blue.

Reference

1. J. Park, K. J. An, Y. S. Hwang, J. G. Park, H. J. Noh, J. Y. Kim, J. H. Park, N. M. Hwang and T. Hyeon, *Nat. Mater.,* 2004, **3**, 891.