

Supporting Information

Sensitive turn-on fluorescent detection of cyanide based on the dissolution of fluorophore functionalized gold nanoparticles

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Experimental Section

Materials. Rhodamine B, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, trisodium citrate, potassium cyanide, 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. Citrate-stabilized Au NPs were prepared following Frens' method with a minor modification.¹ The size of as-prepared Au-NPs was characterized with transmission electron microscopy (TEM), which revealed an average diameter of 13 nm. The concentration of as-prepared Au-NPs was calculated to be approximately 7.1 nM assuming that all gold in the HAuCl_4 was reduced.

Preparation of RB-Au NPs. A stock solution of RB with 2 mM was prepared in water. An aliquot of RB with final concentration of 7.5×10^{-8} M was added into the as-prepared Au NPs solution (0.8 nM) that was prepared in 0.01 M NaOH-NaHCO_3 buffer (pH 10.0). Then the solution was equilibrated at room temperature for half an hour. The resulted mixture solution was denoted as RB-Au NPs, and used for the further cyanide detection. The very low fluorescence observed in RB-Au NPs solution indicated that all the RB had adsorbed effectively onto the surface of Au NPs.

Fluorescence Detection of Cyanide. A 0.12 M stock solution of KCN was prepared in 0.01 M NaOH-NaHCO_3 buffer (pH 10.0), from which various CN^- concentrations were prepared by serial dilution. The stock solutions were used within three days. A

freshly prepared mixture solution containing 7.5×10^{-8} M RB and 0.8 nM Au NPs in NaOH-NaHCO₃ buffer was used for CN⁻ detection, into which KCN with different concentrations were added and equilibrated for 20 min before the spectral measurements. To probe the anion selectivity, the following salts were used: KCN, Na₂B₄O₇, NaBr, KBrO₃, NaCl, NaClO₄, Na₂CO₃, K₂C₂O₄, KF, NaI, KIO₃, NaNO₂, NaNO₃, Na₃PO₄, Na₂S, KSCN, Na₂SO₃, Na₂SO₄, and K₂S₂O₈. A 2.4 mM stock solution was prepared. Subsequently, salt solution with appropriate volume was mixed with the above mixture solution. Then the solution was equilibrated for 20 min before the spectral measurements.

Mechanism Investigation. To verify the first point of our suggested mechanism that RB molecules would possibly desorb from the surface of Au NPs upon the etching by cyanide, the following experiments were conducted. A mixture solution containing 7.5×10^{-8} M RB and 0.8 nM Au NPs in NaOH-NaHCO₃ buffer (0.01 M, pH 10.0) in the presence of 4.5×10^{-5} M KCN was equilibrated at room temperature for 20 min. Then they were centrifuged at 8000 rpm twice to remove undissolved Au NPs. The remaining upper clear solution was subjected to fluorescence measurement, which showed an obvious emission band of RB at 577 nm. Control experiment suggested no visible fluorescence for the sample without adding cyanide under the identical conditions.

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). Each spectrum was the average of three scans. A 1.00 cm path length rectangular quartz cell was used for these measurements. TEM measurements were made on a JEOL 2000 TEM operating at 200 kV. The sample for TEM characterization was prepared by placing a drop of colloidal solution on carbon-coated copper grid and dried at room temperature. All the measurements were carried out at room temperature (293 ± 1 K).

Figures

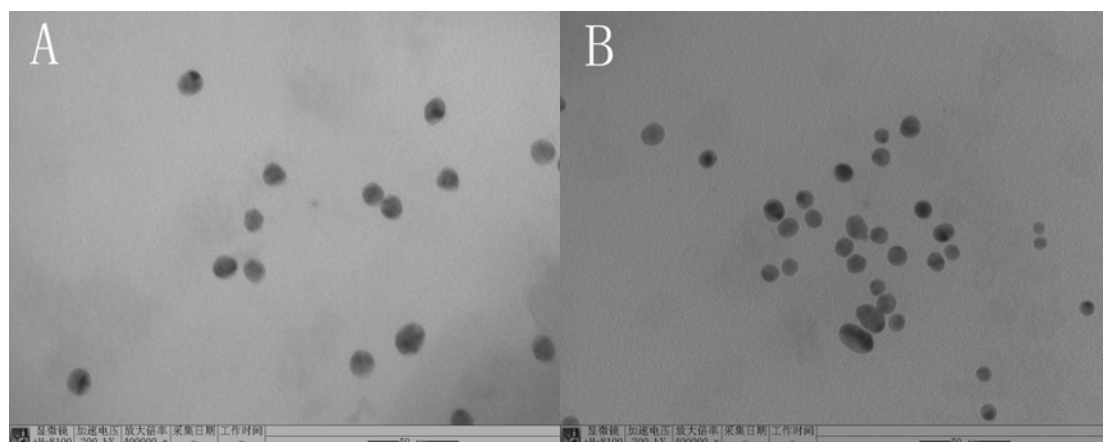


Figure S1. Typical TEM graphs of RB-Au NPs in the absence (A) and presence (B) of 3.0×10^{-5} M cyanide potassium. The average diameters of Au NPs, upon judging from more than 100 individual particles, revealed a decrease from **13** nm to **9.5** nm in the presence of 3.0×10^{-5} M cyanide potassium.

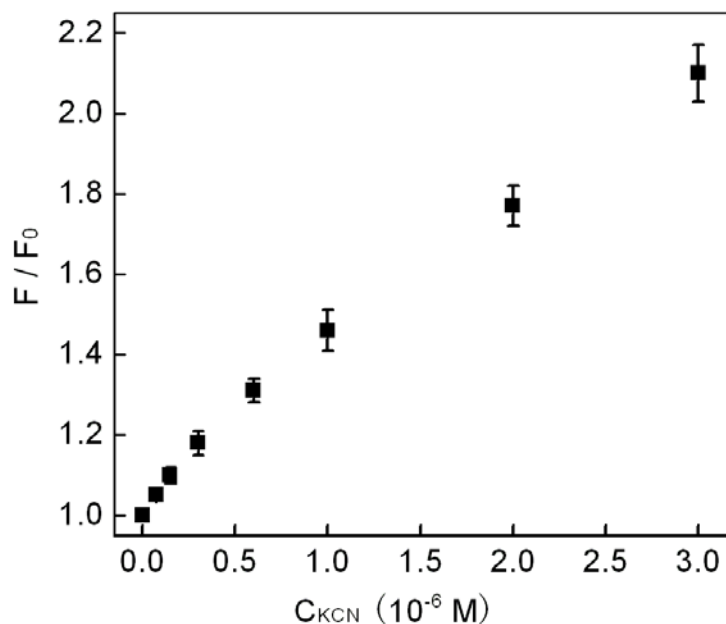


Figure S2. Plots of the relative fluorescence intensity (F/F_0) as a function of the cyanide concentration in the lower concentration range. The error bars represent the standard deviation of three measurements.

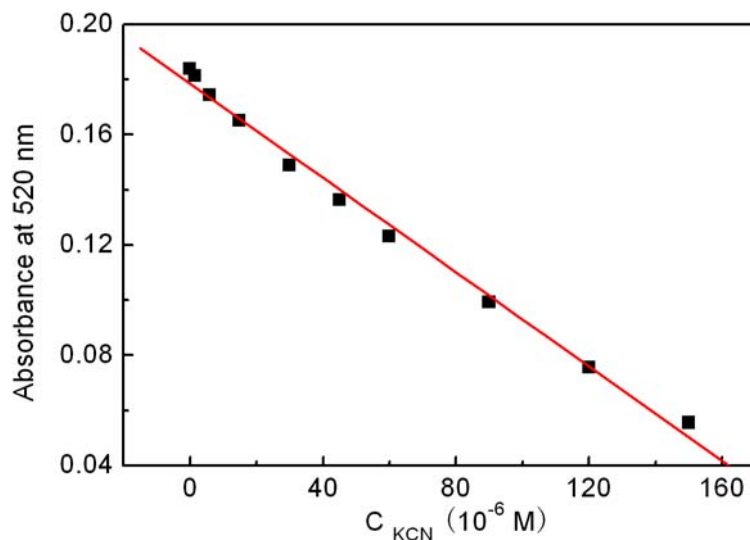


Figure S3. Linear plots of the absorbance of RB-Au NPs at 520 nm versus the concentration of added cyanide potassium.

Discussion on the origin of fluorescence decrease of RB in the presence of Au NPs

The observed fluorescence decrease of RB in the presence of Au NPs can be mainly attributed to the following two origins.

Firstly, since RB is positively charged, it can be adsorbed on the surface of citrate-stabilized Au NPs due to electrostatic interactions, which leads to the formation of RB-Au NPs assembly. Due to the strong quenching ability of Au NPs, fluorescence of RB can be quenched by efficient nonradiative energy transfer to Au NPs.² Such a quenching mechanism is known as *static quenching* (SQ).

Secondly, the absorbance of RB-Au NPs at both the excitation and emission wavelength is substantial (see Figure 2 in the text), which can also cause the fluorescence decrease. Thus the contribution of *inner filter effect* (IFE) to the observed fluorescence quenching can not be neglected.

In order to quantify the relative contribution of SQ and IFE, the fluorescence attenuation due to IFE was calculated by using the method proposed by Leese and Wehry:^{3,4}

$$\frac{F}{F_0} = \frac{1 - 10^{-\varepsilon_{ex}[Q]b}}{2.303\varepsilon_{ex}[Q]b} \quad (1)$$

$$\frac{F}{F_0} = \frac{1 - 10^{-\varepsilon_{em}[Q]b}}{2.303\varepsilon_{em}[Q]b} \quad (2)$$

Where F and F_0 are the fluorescence intensity in the presence and absence of quencher (Q), respectively, ε_{ex} and ε_{em} are the molar absorption coefficients of Q at

excitation and emission wavelength, respectively, and b is the effective path length. For a given measurement, $\varepsilon[Q]b$ can be replaced with A (absorbance), thus the above equations can be further simplified as:

$$\frac{F}{F_0} = \frac{1-10^{-A_{ex}}}{2.303A_{ex}} \quad (3)$$

$$\frac{F}{F_0} = \frac{1-10^{-A_{em}}}{2.303A_{em}} \quad (4)$$

Then the fluorescence decrease caused by the IFE (FD_{IFE}) can be calculated as:

$$FD_{IFE} = FD_{IFE, ex} + FD_{IFE, em} = \left(1 - \frac{1-10^{-A_{ex}}}{2.303A_{ex}}\right) + \left(1 - \frac{1-10^{-A_{em}}}{2.303A_{em}}\right) \quad (5)$$

For the solution containing 7.5×10^{-8} M RB and 0.8 nM Au NPs in NaOH-NaHCO₃ buffer, the absorbance at the excitation wavelength (520 nm) and emission wavelength (577 nm) was measured to be 0.18 and 0.06, respectively. Consequently, FD_{IFE} was calculated to be 24.8%. On the other hand, the observed fluorescence decrease (FD_{OBS}) of RB in the presence of Au NPs was measured to be 93.8% from the fluorescence data. Supposing $FD_{OBS} = FD_{IFE} + FD_{SQ}$, where FD_{SQ} is the fluorescence decrease caused by static quenching, then the relative contribution of IFE and static quenching to the fluorescence quenching can be roughly estimated as 26.4% ($\frac{FD_{IFE}}{FD_{OBS}}$), and 73.6% ($1 - \frac{FD_{IFE}}{FD_{OBS}}$), respectively.

It is obvious from the above analysis that both static quenching and IFE contributed to the observed fluorescence decrease of RB in the presence of Au NPs, while the former was the dominant factor.

Reference:

- [1] G. Frens, *Nat. Phys. Sci.*, 1973, **241**, 20.
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- [3] R. A. Leese and E. L. Wehry, *Anal. Chem.*, 1978, **50**, 1193.
- [4] P. Yuan and D. R. Walt, *Anal. Chem.*, 1987, **59**, 2391.