Silver Nanoclusters with Enhanced Fluorescence and Specific ion Recognition Triggered by Alcohol Solvents: A Highly Selective Fluorimetric Strategy for Iodide Ions in Urine

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Abstract

Supporting information includes the experimental details and data. The experimental section includes the materials and instruments, the preparation and dispersion of AgNCs, the optimization of detection conditions, fluorimetric measurement procedure for iodide ions, and fluorimetric analysis of practical samples. Data are provided for the comparable stability investigation, the optimization of IPA-to-water ratios, the DLS measurement, the optimization of analysis conditions, fluorimetric analysis of I⁻ ions in buffer and urine samples, and comparison of detection performances among different fluorimetric methods.

EXPERIMENTAL SECTION

Experimental section

Materials and Instruments

Sodium borohydride (NaBH₄), α-lipoic acid (LA), glutathione (GSH), and silver nitrate (AgNO₃) were purchased from Sigma-Aldrich (Beijing, China). Potassium iodide (KI) and other inorganic anions salt were purchased from Beijing Chemical Reagent Co (Beijing, China).
Methanol, ethanol, isopropanol (IPA), n-propyl alcohol, ethylene glycol, dimethyl formamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofuran (THF), and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The urine samples were kindly provided by the local hospital. All of the chemicals are of analytical grade, and all glass containers were cleaned by aqua regia and ultrapure water before usage.

Transmission electron microscopy (TEM, Tecnai G20, FEI, USA) imaging operated at 100 kv were employed to characterize the morphology of AgNCs in IPA before and after adding I⁻ ions. UV-3600 spectrophotometer (Shimadzu, Japan) was used to measure the UV-vis spectra, displaying AgNCs in different solvents as well as AgNCs in the media of water and IPA with or without I⁻ ions. Fluorescent emission spectra of AgNCs in IPA were obtained by fluorescence spectrometer (Horiba, FluoroMax-4, Japan) at the excitation wavelength of 425 nm on a slit of 5.0 nm. The photographs of corresponding reactions products were recorded under UV light at exciting wavelength of 365 nm. A dynamic light scattering (DLS, Malven Instruments, Britain) apparatus was used to measure the hydrodynamic diameters of AgNCs in the absence and presence of I⁻ ions. Moreover, Table centrifuge (Thermo Scientific, Deutschland) was used in the preparation and purification procedures.

Preparation and dispersion of AgNCs

AgNCs were synthesized in aqueous media according to our previous work using GSH as a ligand agent for the passivation working with the template of dihydrolipoic acid (DHLA) at room temperature. Typically, under vigorously stirring, an aliquot of 20 mM AgNO₃ (125 μL) and 50 mM GSH (150 μL) were introduced into 5.0 mL water, followed by the adjustment of pH value to 9.0 using 1.0 M NaOH. Moreover, an aliquot of 5.0 mg LA was mixed with NaBH₄ in 1.0 mL water at a molar ratio of LA : NaBH₄ = 4 : 1 to be stirred till a clear solution appeared, yielding the DHLA. Then, the DHLA solution was added into the AgNO₃-GSH mixture above to be vigorously stirred for 20 min. After being further incubated for about 1.5 h at room temperature, the resulting mixture of AgNCs was purified by dialysis for 12 h to be stored in dark at 4 °C.

A certain amount of AgNCs were dispersed separately into various solvents including methanol, ethanol, IPA, n-propyl alcohol, ethylene glycol, DMF, DMSO, THF, and acetone. The fluorescence intensities were recorded for the comparison studies on the solvent-enhanced fluorescence of AgNCs.
Fluorimetric assays for iodide ions

The optimization of the detection conditions were optimized for the developed the fluorimetric assay for I\(^{-}\) ions, including the dosages of AgNCs (0.060, 0.070, 0.084, 0.105, 0.140, and 0.209 mM), pH values (4.0, 6.0, 7.0, 8.0, 10, and 12), ionic strengths (0.0, 50, 100, 150, 200, 250, 250, and 300 mM NaCl), and reaction time (1.0, 2.0, 3.0, 5.0, 8.0, and 10 min).

The fluorimetric assays for I\(^{-}\) ions were conducted with AgNCs in water containing IPA by the following procedure. A certain amount of I\(^{-}\) ions solution at different concentrations (0, 0.0010, 0.0050, 0.010, 0.050, 0.10, 0.50, 1.0, 5.0, 10 \(\mu\)M) were separately mixed with an aliquot of AgNCs (0.105 mM) in IPA-containing buffer to be stirred for 5 min. The fluorimetric measurements were then performed by recording the changes of fluorescence spectra.

According to the same procedure above, the developed fluorimetric assay was applied to probe I\(^{-}\) ions spiked in urine samples with different I\(^{-}\) levels (0, 0.010, 0.050, 0.10, 0.50, 1.0, 2.5, 5.0, 7.5, 10 \(\mu\)M). Also, the control tests for different inorganic anions of 1.0 \(\mu\)M (Cl\(^{-}\), HPO\(_4^{2-}\), H\(_2\)PO\(_4^{+}\), SO\(_4^{2-}\), Ac\(^{-}\), C\(_2\)O\(_4^{2-}\), CO\(_3^{2-}\), HCO\(_3^{2-}\), Br\(^{-}\), IO\(_3^{-}\), NO\(_3^{-}\), S\(^2-\), and F\(^{-}\) ions) were conducted accordingly. Herein, the quenching efficiencies were calculated according to the following equation: quenching efficiencies = \((F_0 - F)/F_0\), where \(F_0\) and \(F\) refer to the fluorescence intensities of the Ag NCs in water containing IPA in the absence and presence of I\(^{-}\) ions, respectively.
Fig. S1 (A) The relative FIs of AgNCs dispersed in water (a) with and (b) without IPA over different time intervals stored at 4 °C; (B) the fluorescence quenching efficiencies of AgNCs in water and different alcohol solvents before and after the addition of I− ions (5.0 μM).
**Fig. S2** The IPA-to-water volume ratios-depending fluorescence intensities (FIs) of AgNCs, where the relative fluorescence intensities ($F/F_0$) were calculated from $F$ and $F_0$ that refer to the FIs of AgNCs in water with and without IPA, respectively.
Fig. S3 Hydrodynamic diameters of AgNCs in water containing IPA in the (A) absence and (B) presence of I- ions (5.0 µM) measured by DLS.
**Fig. S4** The FIs of AgNCs in IPA depending on (A) the AgNCs concentrations in the (a) presence and (b) absence of 1.0 μM I− ions (inset: quenching efficiencies versus AgNCs concentrations), (B) pH values, (C) ion strengths of different NaCl concentrations, and (D) time of the reaction between AgNCs and I− ions.
**Fig. S5** Fluorescence spectra of AgNCs in IPA-containing water upon the addition of I⁻ ions of different concentrations separately spiked in (A) buffer and (C) urine; corresponding to their calibration curves (B and D) of the fluorescence quenching efficiencies versus the logarithmic concentrations of I⁻ ions (insert: photographs of tested solutions under UV light). The fluorescence spectra were recorded at the excitation wavelength of 425 nm.
Table S1 Comparison of detection performances for I⁻ ions among different fluorimetric methods using different fluorescent probes

<table>
<thead>
<tr>
<th>Fluorescent probes</th>
<th>LODs (nM)</th>
<th>Linear ranges (μM)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgNCs</td>
<td>7.50</td>
<td>0.010-10</td>
<td>This work</td>
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<tr>
<td>Oligopyrrole derivatives</td>
<td>90.0</td>
<td>0.10-6.0</td>
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<td>Carbon nitride Qdots</td>
<td>2500</td>
<td>0.50-30</td>
<td>Ref. 2</td>
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<tr>
<td>CdSe Qdots</td>
<td>280</td>
<td>4.5-35</td>
<td>Ref. 3</td>
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