Supporting Materials

Boiling Water Synthesis of Ultrastable Thiolated Silver Nanoclusters with Aggregation-Induced Emission

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EXPERIMENTAL SECTION

1. Materials

Ultrapure water (18.2 MΩ) was used throughout the study. All glassware and magnetic stir bars were washed with aqua regia, rinsed with abundant ethanol and ultrapure water, and dried in an oven before use. All chemicals were commercially available and used as received: silver nitrate (AgNO₃) and sodium hydroxide (NaOH) were purchased from Merck. L-glutathione reduced (GSH) was purchased from Sigma-Aldrich.

2. Instruments

UV-vis absorption and photoluminescence (PL) spectra were recorded by a Shimadzu UV-1800 photospectrometer and a PerkinElmer LS-5S fluorescence spectrometer, respectively. Photoluminescence lifetimes were measured by time-correlated single-photon counting (TCSPC) on a Horiba JobinYvon Fluorolog-3 spectrofluorometer with a pulsed light-emitting diode (LED) (438 nm, pulse duration <1 ns) as the excitation source. The molecular formulas of the Ag NCs were determined by electrospray ionization-mass spectrometry (ESI-MS) on a Bruker microTOF-Q system. Native polyacrylamide gel electrophoresis (PAGE) was carried out on a Bio-Rad Mini-Protean Tetra Cell system using discontinuous gels (1.0 × 83 × 73 mm). 30 and 4 wt% acrylamide monomers were prepared for resolving and stacking gels, respectively. The electrophoresis was allowed to run for ~3 h at a fixed voltage of 170 V at 4 °C. Transmission electron microscopy (TEM) images of the Ag NCs were taken on a JEOL JEM-2010 microscope operating at 200 kV. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos AXIS UltraDLD spectrometer (Kratos Analytical Ltd).

3. Synthesis of Highly Luminescent GSH-Protected Ag NCs

Freshly prepared aqueous solutions of GSH (300 μL, 50 mM) and AgNO₃ (250 μL, 20 mM) were mixed in ultrapure water (4.45 mL) under vigorous stirring (1100 rpm) at room temperature to form GSH-Ag(I) complex, which was a white precipitate at pH 3.0. After that, NaOH solution (180 μL, 0.1 M) was added drop wise to adjust the pH to 6.1. Within several seconds, the white precipitate was dissolved and the solution was turned to colorless. The vessel was then sealed airtight and placed on a hot plate for heating. The solution in the
vessel was boiling under vigorous stirring for about 5 hours. During the heating process, the solution was changed from colorless to light yellow and finally to yellowish brown. Without further stirring, the solution of Ag NCs was incubated at refrigerator (4 °C) for ~12 h. After incubation, highly red-emitting Ag NCs were obtained as the final product.

Fig. S1 A representative TEM image of the as-synthesized luminescent Ag NCs.

Fig. S2 X-ray photoelectron spectroscopy (XPS) spectrum of Ag 3d species of the as-synthesized luminescent Ag NCs (black line). The spectrum was deconvoluted into Ag(0) (367.7 eV, dashed blue line) and Ag(I) components (367.9 eV, dashed red line).
**Fig. S3** Photoemission spectra ($\lambda_{ex} = 420$nm) of the as-synthesized luminescent Ag NCs in various conditions: (1) in water at room temperature (black line), (2) in water at 90 °C (red line), (3) in 30 mM HEPES buffer solution (green line), and (4) in 0.1 M NaCl solution (blue line).

**Fig. S4** Digital photos of the luminescent Ag NCs synthesized in a 250 mL round-bottom flask under visible (left) and UV (right) light.
**Fig. S5** UV-vis absorption spectrum (black line) and photoemission spectrum (red line, $\lambda_{ex} = 420$ nm) of the product synthesized at 90 $^\circ$C. The inset shows photographs of the product under visible (left) and UV (right) light.

**Fig. S6** UV-vis absorption (black line) and photoemission spectrum (red line, $\lambda_{ex} = 420$ nm) of the Ag NCs synthesized under the condition of pH = 7. The inset shows photographs of the Ag NCs under visible (left) and UV (right) light.
**Fig. S7** UV-vis absorption (black line) and photoemission spectrum (red line, $\lambda_{ex} = 420$ nm) of the Ag(I)-SG complexes under pH = 6.1. The insets are photographs of the Ag(I)-SG complexes under visible (left) and UV (right) light.