Sonochemical synthesis of highly fluorescent glutathione-stabilized Ag nanoclusters and S\textsuperscript{2-} sensing

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Experimental Section

Chemicals.

L-Glutathione (GSH, reduced, 99\%) was purchased from Sigma-Aldrich. Silver nitrate (ACS, 99.9+\%) was purchased from Alfa Aesar. All chemicals were used without further purification. Ultra-pure water with a resistivity 18.2 M\(\Omega\) cm obtained from a Millipore purification system was used for the experiments.

Synthesis of Ag nanoclusters (AgNCs).

Briefly, 21.2 mg AgNO\textsubscript{3} dissolved in 5.0 mL water was slowly added to 153.6 mg GSH in 20 mL water with vigorous stirring. The solution became turbid due to the formation of a silver thiolate suspension\textsuperscript{1}, then the pH was adjusted by dropwise addition of a 1 M solution of NaOH until the turbid solution became clear (pH~5.0). The mixture was irradiated with ultrasound (Ultrasonic Cleaner AS2060B, 40 KHz, 60 W) in the dark for different times.

Characterization

UV-Vis absorption and fluorescence spectra were obtained with a UV2300 spectrophotometer (Techcomp) and a F-4500 spectrophotometer (Hitachi), respectively. 0.9 mL AgNCs solution without post-preparative treatment was diluted with 2.1 mL water for recording the spectra. Transmission electron microscope (TEM) images and energy dispersive X-ray (EDX) spectra were collected using a TECNATI F-30(Netherlands). FT-IR spectra were recorded with a Nicolet 380
spectrophotometer. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrum analysis with positive-ion mode was conducted with a Bruker Daltonics - microflex MALDI TOF-MS. The MALDI sample was prepared by mixing dialyzed AgNCs with an equal volume of α-cyano-4-hydroxycinnamic acid.

References

**Fig. S1** The stability of the as-prepared fluorescent AgNCs at different storage time.

**Fig. S2** Emission spectra of fluorescent AgNCs prepared by sonochemical synthesis with different excitation wavelengths from 320 to 370 nm.
Fig. S3 UV-Vis absorption spectra (a) and emission spectra (b) of fluorescent AgNCs under different ultrasonic irradiation times. The excitation wavelength was 350 nm.
Fig. S4 UV-Vis absorption spectra (a) and emission spectra (b) of fluorescent AgNCs prepared by sonochemical synthesis with different ratios of Ag⁺ to GSH.
Fig. S5 UV-Vis absorption spectra (a) and emission spectra (b) of fluorescent AgNCs prepared by sonochemical synthesis under different pH conditions.
Fig. S6 UV-Vis absorption spectra of fluorescent AgNCs in the presence of different concentrations of $S^2\text{-}$.

Inset: photographs of fluorescent AgNCs in the presence of different concentrations of $S^2\text{-}$.