Supporting Information

Synthesis of Ag nanoclusters by pH-dependent etching method in the aqueous solution

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Experimental

Materials.

Silver nitrate ($AgNO_3$) was purchased from BIO BASIC INC. The gelatin (type A, bloom 300) and sodium borohydride were obtained from Sigma–Aldrich. The lipoic acid was purchased from Tokoy Chemical Industry (TCI). All other reagents were of analytical reagent grade, and used as received. Deionized water purified by a Milli-Q Water Purification System (Millipore, Bedford, MA, USA) with a resistance of 18.2 MΩ cm was used throughout the experiment.

Preparation of Ag nanoparticles (AgNPs)

AgNPs was prepared by chemical reduction method using sodium borohydride as reductant. In brief, 55 mg of gelatin powder was first dissolved in 10 mL water. Then, 100 μL $AgNO_3$ with a concentration of 10 mM was added into the gelatin solution and mixed thoroughly. Afterward, 100 μL sodium borohydride aqueous solution (50 mM) was added into the mixture and stirred at room temperature 37 ^{o}C for 24 h. During this period, the colorless mixture gradually became dark brown, and finally turned into yellowish orange.

Preparation of fluorescent Ag nanoclusters (AgNCs)

Fluorescent AgNCs were prepared by etching the above AgNPs with reduced lipoic acid (DHLA). First, reduced DHLA was prepared by introducing 100 μL of 50 mM dilute aqueous sodium borohydride solution into a freshly prepared 10 mL of 5 mM lipoic acid solution and stirring for about 30 min at room temperature. Then, 1 mL of freshly prepared aqueous DHLA solution were added to freshly prepared 9 mL of Ag nanoparticle aqueous solution to produce AgNCs. During the latter period, the color of the mixture changed to colorless gradually.

Photoluminescence (PL) measurement: The fluorescence of AgNCs was recorded on an F-4600 spectrophotometer (Hitachi) at room temperature. The AgNCs aqueous solution (200 μL) loaded into quartz cuvette has been excited at 380 nm wavelength and emission scans have been recorded from 400 to 700 nm using a slit width of 5 nm for analysis. The excitation spectra were measured at the corresponding maximum emission wavelength using the same slit width. The quantum yield of an unknown fluorophore (unknown) has been determined using the parker-rees method (Phys. Chem., 1992, 40, 445–450; Chem. Phys. Lett., 1994, 218, 115–121; J. Phys. Chem. B, 1998, 102, 10667–10671; J. Am. Chem. Soc., 1990, 112, 4657–4664.).

The quantum yield was measured by a relative comparison method using the following equation:

$$\Phi_{unk} = \frac{A_{std}}{A_{unk}} \times \frac{F_{unk}}{F_{std}} \times \frac{n_{unk}^2}{n_{std}^2} \times \Phi_{std}$$

Φ = Quantum yield; unk = Unknown sample;
std = Standard; n = Refractive index of solvent;
A = Absorption at the selected excitation wavelength;
F = Integrated fluorescence signal in the emission region.

Here, in our study we measured series of the samples and the standard quinine sulfate (Φ = 58%, 0.1 M H_2SO_4) to calculate the quantum yield of AgNCs. The emission spectra were recorded on F-4600 spectrophotometer (Hitachi) under the excitation of 380 nm light for Ag NCs.

UV-Vis spectroscopy: UV-Vis spectra were carried out on a UV 2450 spectrophotometer (SHIMADZU). The aqueous AgNCs solutions (500 μL) were analyzed in a 1 cm path length quartz cuvette at room temperature. The formation of AgNCs was spectroscopically monitored over the wavelength range of 200-700 nm.

Fluorescence lifetime: Fluorescence lifetime measurements were performed on a Fluo Time 100 TCSPC fluorescence platform from Picoquant GmbH (Berlin, Germany). A pulsed LED source (375 nm) was used to excite the clusters.

Transmission electron microscope (TEM): TEM images and energy dispersive X-ray (EDX) were recorded on a TECNAI F-30 (Netherlands) operating at an acceleration voltage of 200 kV. TEM samples were prepared by dropping a diluted water solution of AgNCs onto carbon-coated copper grids (400 mesh) and dried in laboratory ambience.

Fourier-transform infrared (FT-IR) spectra: FT-IR spectra were measured with a Perkin Elmer Spectrum One instrument. KBr crystals were used as the matrix for sample preparation.

Chemical photostability: The effect of metal ions on the fluorescence of AgNCs was investigated as follows. First, Cd^{2+}, Ba^{2+}, Co^{2+}, Sr^{2+}, Pb^{2+}, Mn^{2+}, Fe^{2+}, Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Ni^{2+}, Mg^{2+}, Ag^+ and Hg^{2+} nitrates or chlorides solutions (0.2 mM) were prepared. Then the fluorescent AgNCs were added into the each solution and the final concentration of AgNCs was 30 μM. The fluorescence of mixtures was immediately measured using F-4600 spectrophotometer (Hitachi) equipped with a high-power Xenon lamp.
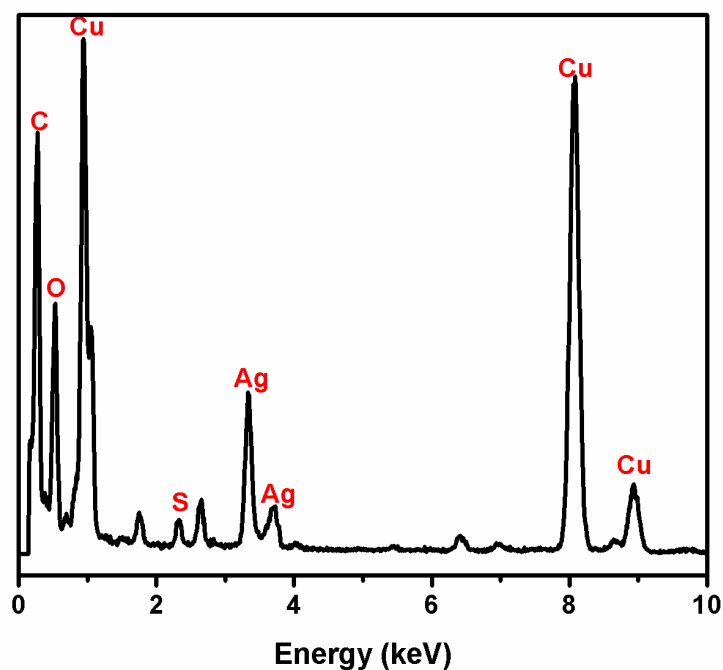
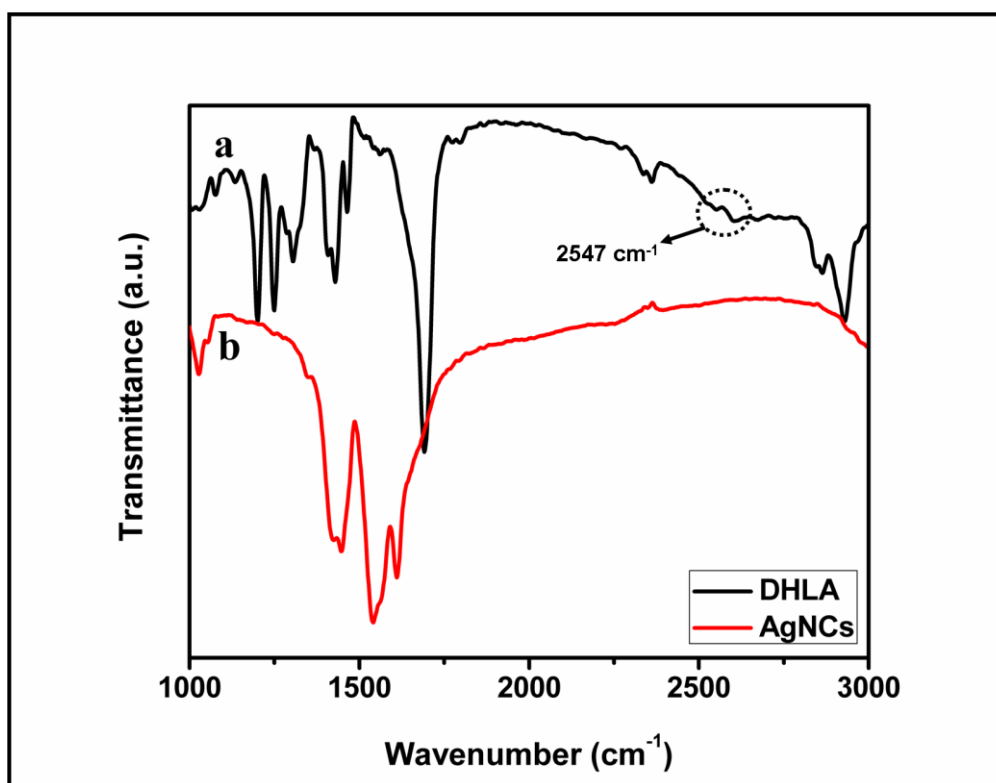*Figures*

Figure S1 EDX spectrum of the fluorescent AgNCs.

Figure S2 FT-IR spectra of (a) dihydrolipoic acid (DHLA) and (b) DHLA-stabilized AgNCs
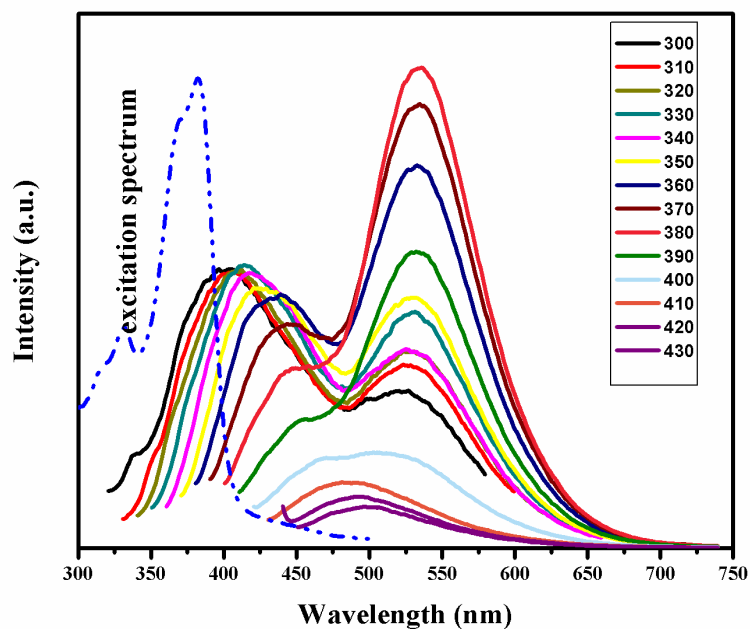

Figure S3 Emission spectra of fluorescent AgNCs with different excitation wavelengths from 300 to 430 nm.
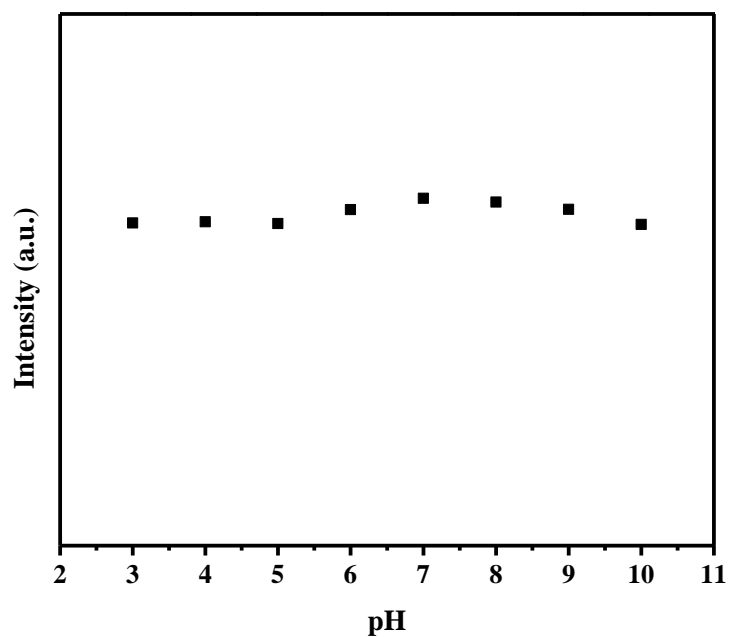
Figure S4   Fluorescence intensity of AgNCs measured at 530 nm as a function of pH[a]

[a]The AgNCs solution was diluted by 10 mM phosphate buffered saline (PBS), then the pH was adjusted by 0.1 M HCl and NaOH
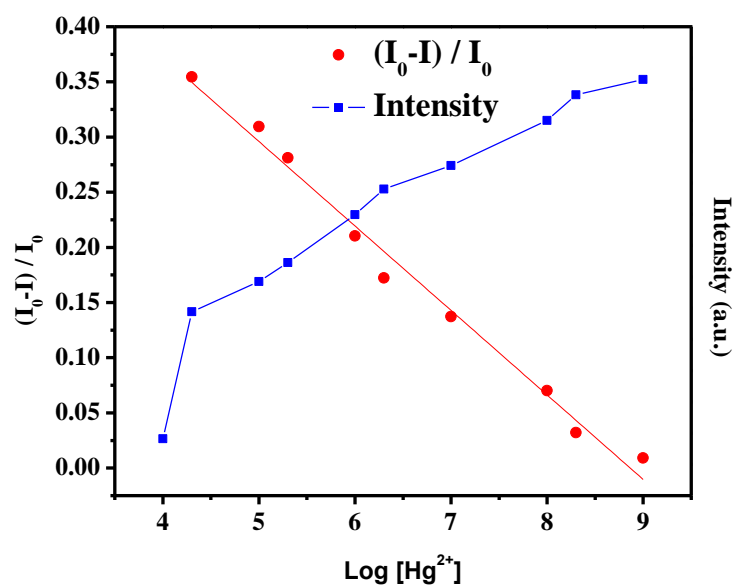

Figure S5 The Stern/Volmer plot of fluorescent quenching and relative fluorescence intensity at 530 nm against Hg^{2+} concentration.

Table S1 Comparison of fluorescent metallic nanoclusters via biomolecule-directed approaches

Nanoclusters	Ligands	Emission	Quantum yield	Applications	Ref.
AgNCs	DHLA	680 nm[1] 652 nm[2]	0.024%[1] 2%[2]	n.r. Hg^{2+} detection[2]	[1, 2]
AgNCs	GSH	660 nm[3] 430 nm[4]	15%[3] 1.9%[4]	Hg^{2+} detection[3]; S^{2-} detection[4]	[3, 4]
AgNCs	LA-PEG-X	680 nm	~3.3%	n.r.	[5]
AgNCs	dBSA	637 nm	~1.2%	Hg^{2+} detection	[6]
AgNCs	lysozyme	605 nm	1.3%	Hg^{2+} detection	[7]
AgNCs	DNA	615 nm	~18.6%	Detection of thiol compounds[8];	[8]
AgNCs	PMAA	575 nm[9]; 420-626 nm[10]	<1%[9]	Cr^{3+} sensing[9]	[9, 10]
AgNCs	PAA	575 nm	n.r.	Hg^{2+} detection	[11]
AuNCs	DHLA	650 nm	1.83±0.32%	Cell imaging	[12]
AuNCs	BSA	450 nm[a], 680 nm[b]	6.07%[a], 5.53%[b]	n.r.	[13]
AuNCs	dipeptide[c]	410 nm	41.25%	As^{3+} sensing	[14]

AgNCs, silver nanoclusters; **AuNCs**, gold nanoclusters; **DHLA**, dihydrolipoic acid; **GSH**, glutathione; **LA**, lipoic acid; **PEG**, polyethylene glycol; **X**=NH_2, COOH, $COOCH_3$; **dBSA,** denatured bovine serum albumin; **PMAA**, polymethacrylic acid sodium salt; **PAA**, poly(acrylic acid); **n.r.**, not reported; **Ref.**, references.

[a] Au_8-BSA; [b]Au_{25}-BSA; [c] L-cysteinyl-L-cysteinyl

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