Supporting information for

Synthesis of fluorescence Ag nanoclusters and their application in α-L-fucosidase detection

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Experimental Section

Materials

Poly (methacrylic acid, sodium salt) (PMAA) solution (30 wt% solution in water) and 2-chloro-4-nitrophenyl- α -L-fucopyranoside (CNP-AFu, DZ082B-R1) were purchased from Sigma. The enzyme α -L-fucosidase (AFu, DZ082B, EC 3.2.1.51) were purchased from Seebio Biotechnology Inc. Silver nitrate (AgNO₃) was obtained from Beijing ShiJi Company. Phosphate buffered saline (PBS) was prepared: 1.02 mM Na₂HPO₄, 6.45 mM KH₂PO₄, pH 7.01. The reagents such as AgNO₃, Na₂HPO₄, KH₂PO₄ and cadmium nitrate were of analytical reagent grade. The ultrapure water (0.22 µm) was produced using a Millipore-Q water system.

Synthesis of Ag nanoclusters

During this experiment, PMAA and silver nitrate solution was mixed in a 3 mouth flask with nitrogen incoming to prepare fluorescent Ag nanoclusters (NCs). In first step, PMAA was diluted by water in the proportion of 1:20 to acquire a solution A and AgNO₃ is reduced in water to acquire 12.5 mM AgNO₃ solution (solution B). 80 mL solution B was heated at 90 °C. Then, 9 mL solution A was added quickly to the hot solution B. At first, the mixture gradually became colorless to light umber color, and then a reddish purple color was developed after 270 min. Transmission electron microscope (TEM) images also suggest that the Ag NCs have a narrow size distribution. The average size of the Ag NCs was about 1.7 nm. The main absorption peak in the UV/vis spectrum appeared at 510 nm. Photoluminescence spectrum (PL spectrum) shows an emission maximum at 610 nm upon excitation at 510 nm.

Instrumentation

Fluorescence measurements were carried out on a Cary Eclipse fluorescence

spectrophotometer (Varian, Inc.). The emission spectra of Ag NCs were recorded upon excitation at 510 nm. The exciting slit and the emission slit were 10 and 5 nm, respectively. The samples for the fluorescence measurements were placed in a 10 mm optical path length quartz fluorescence cuvette.

TEM was performed on a JEOL JEM 2010F electron microscope operating at 200 kV. UV-vis spectra were recorded using a JASCO V-570 spectrophotometer at room temperature.

Fluorescence detection of AFu

The AFu detection procedure was described as follows: Detection procedure by Ag NCs: 20 μ L of Ag NCs were diluted into 400 μ L, and then reacted with different concentrations of AFu solution (concentration from 0.01 to 0.5 U/L). The time of the sample preparation was 1 min. The fluorescence intensity of Ag NCs showed a tendency toward stabilization after 5 min (see the Supporting Information Fig. S3). So the detection of AFu was fixed at 5 min.



Figure S1 Size distribution histogram of the Ag NCs prepared with N2 incoming.



Figure S2 The TEM image of Ag NCs prepared without N_2 incoming (3.6 nm in average diameter).



Figure S3 Fluorescence emission spectra of freshly prepared Ag NCs (a) and the placed on one year Ag NCs (b).



Figure S4 Time dependent fluorescence intensity (counts/0.1s) of Ag NCs when illuminated by a

510 nm laser.



Figure S5 Time-dependent fluorescence changes of Ag NCs in water with the presence of 0.2 U/L

AFu: 5 min, 10 min.



Figure S6 (A) TEM images of Ag NCs before AFu was added. Scale bar 10 nm. (B) TEM images of Ag NCs after 0.2 U/L AFu was added. Scale bar 10 nm. (C) TEM images of 0.2 U/L AFu with 12.5 mM AgNO₃. Scale bar 50 nm.

standard).

Method	System	Quantum yield	Reference
		(%)	
Wet chemistry	BSA	1.46	Le Guével et al. ⁽¹⁾
Rapid			
microwave-assisted approach	PMAA	6	Liu et al. ⁽²⁾
			Udaya
Interfacial			Bhaskara Rao
synthesis	H2MSA thiol	3 and 9	et al. (3)
Electrostatically			
Induced Reversible			Yuan et al. ⁽⁴⁾
Phase Transfer	CTAB/TMAD	6.5	
Sonochemical	PMAA	11	Xu et al. ⁽⁵⁾
Wet chemistry	PMAA	13.53	This paper

Table S1 Quantum yield of Ag NCs synthesized by different methods (using Rhodamine 6G as

(1) X. Le Guével, B. Hotzer, G. Jung, K. Hollemeyer, V. Trouillet and M. Schneider, *J. Phys. Chem. C*, 2011, **115**, 10955.

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Method	System	Limit of detection	Reference
		(U L ⁻¹)	
Potentiometric	2-Chloro-4-PNP-Rd	1	Othman et al.
	PVC		(1)
	membrane sensor		
Spectrofluorimetric	The ion associated	0.1	El-Shahawi
	of rhodamin-B		et al. ⁽²⁾
	(RB ⁺ CNP ⁻)		
HPLC	HPLC of p-NP	0.1	Noni et al. ⁽³⁾
Fluorescence	QDs enzyme	0.01	Chen et al. ⁽⁴⁾
Fluorescence	Ag NCs	0.001	This paper

Table S2 Detection limits of AFu by different sensor systems.

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- (4) Z. Z. Chen, X. L. Ren, X. W. Meng, Y. Q. Zhang, D. Chen and F. Q. Tang, *Anal. Chem.*, 2012, 84, 4077.